Rhythmic Growth of Target and Spiral Spherulites of Crystalline Polymer Blends

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(Received 26 March 1999)

Numerical calculations reveal that the target and spiral growth patterns in spherulites can be generated from the time-dependent Ginzburg-Landau equations (model *C*) by coupling a conserved compositional order parameter and a nonconserved crystal ordering parameter. Of particular interest is that the periodic concentric rings (target) or the spirals at the spherulitic core remain stationary in both the crystal (orientational) ordering field and the concentration field. Another intriguing observation is that the growth of target and spiral spherulites occurs in a stepwise fashion in synchronism with the rhythmic energy dissipation during crystallization.

PACS numbers: 61.41.+e, 64.70.Dv, 81.10.Aj

Spiral and target patterns are commonly observed in excitable media and nonlinear dissipative systems involving chemical waves, liquid crystal ordering, and biological organization [1]. Similar spiral and target patterns have also been found experimentally during crystallization of polymers, organic, and inorganic materials [2–5]. One major difference is that the core of the spiral crystal is stationary as opposed to the excitable media where the core is constantly oscillating. Although a similarity in patterns does not automatically guarantee that the origin is the same, it is worth investigating the pattern forming aspects of polymer crystallization from a new perspective of phase transitions.

In atomic crystals, crystallization phenomena have been generally analyzed in the context of the classical macroscopic models of phase transitions [6,7]. The governing equations treat thermodynamic variables, such as temperature and composition of the individual phases, independently with a discrete interface of zero thickness. The discontinuity in the thermodynamic variables and in the gradients often presents difficult mathematical formulations and numerical singularities [8]. Recently, a new microscopic theory has been proposed, often known as a phase-field model [8,9], by incorporating the free energy functional for a crystal phase transition into the time-dependent Ginzburg-Landau-equation model *C* (TDGL model *C*) [10–12]. This phase-field model has been employed in the growth of atomic crystals and recently extended to the phase transitions of binary metal alloys [10] and eutectic crystal growth [13].

The present paper is a first attempt to analyze the pattern forming aspects of polymer crystallization in the context of the TDGL model *C* equations [11,12] pertaining to phase transitions. The purpose of this paper is to demonstrate that the target and spiral growth patterns in polymer spherulites can be generated from the TDGL model *C* equations. In this model, we consider the system as a whole by defining the crystal ordering as a phase field to characterize the phase (or state) of the system at each point in time (*t*) and space (*r*). We then couple the conserved concentration (or number density) and nonconserved orientational order parameters in the coupled TDGL model *C* equations in conjunction with the Landau-type double-well potential with respect to the crystal order parameter.

The TDGL model *C* equations are basically two nonlinear diffusion equations in which a conserved compositional order parameter (ϕ) is coupled with a nonconserved orientational crystal order parameter (ψ), viz. [11,12],

$$\frac{\partial \phi}{\partial t} = \Gamma_\phi \nabla^2 \frac{\delta F(\phi, \psi)}{\delta \phi}, \qquad (1)$$

$$\frac{\partial \Psi}{\partial t} = -\Gamma_\psi \frac{\delta F(\phi, \psi)}{\delta \psi}, \qquad (2)$$

where Γ_ϕ and Γ_ψ are mobilities. In view of the inherent anisotropic topology of chain molecules, it is not far-fetched to regard polymer crystals as anisotropic (for simplicity, the ordering will be treated in a scalar form). Physically, it makes sense to couple the compositional ordering for a polymer blend (or number density for a pure polymer) and the orientational ordering of crystalline molecules. The total free energy density functional of phase ordering, $F(\phi, \psi)$, is given as

$$F(\phi, \psi) = \int \left[f_{\text{comp}}(\phi) + f_{\text{cryst}}(\psi) + f_{\text{coupling}}(\phi, \psi) \right.$$

$$\left. + \tfrac{1}{2} \kappa_\phi |\nabla \phi|^2 + \tfrac{1}{2} \kappa_\psi |\nabla \psi|^2 \right] dr, \qquad (3)$$

in which the compositional ordering may be expressed in terms of the usual Landau-type double-well potential, viz. [10,12],

$$f_{\text{comp}}(\phi) = \frac{r}{2} \phi^2 + \frac{u}{4} \phi^4, \qquad (4)$$

where $r = a(T - T_c)$. The sign of r determines whether the potential has a single-well or a double-well

structure. Furthermore, the orientational crystal ordering may be described as follows [10]:

$$f_{\text{cryst}}(\psi) = W \int_0^{\psi} \psi(\psi - 1)\left[\psi - \tfrac{1}{2} - \theta(T)\right] d\psi,$$
(5)

where W is a dimensionless constant, $\theta(T)$ is a monotonic increasing function of temperature (T), and $|\theta(T)| < \tfrac{1}{2}$ with $\theta = 0$ at the melting temperature T_m. If $T < T_m(-\tfrac{1}{2} < \theta < 0)$, the melt is metastable and the free energy density of crystal ordering has a global minimum at $\psi = 1$. Hence, the solid crystal is the stable phase as it has the lowest free energy. On the other hand, when $T > T_m(0 < \theta < \tfrac{1}{2})$, the crystalline state becomes metastable as the global minimum of the free energy is located at $\psi = 0$, which corresponds to a stable liquid phase. The free energy peak signifying the instability of the system is bound between the metastable melt at $\psi = 0$ and the stable crystalline state at $\psi = 1$. The topology of the double-well potential can be varied on the basis of a single parameter, $\theta(T)$. Further, the magnitude and location of the unstable free energy peak can be related directly to the heat of fusion ΔH_m and supercooling $\Delta T = T - T_m$, i.e., $W\theta(T) = (\Delta H_m/6)(\Delta T/T_m)$ [10].

In practice, the compositional ordering and the orientational crystal ordering do not occur independently during crystallization. These two processes are coupled in some manner, which may be represented by a coupling term composed of a linear and/or quadratic dependence of order parameters as follows;

$$f_{\text{coupling}} = -\psi\phi(\alpha_1 + \alpha_2\phi),$$
(6)

where α_1 and α_2 are coupling constants. In order to determine the temporal evolution of these two order parameters, the total free energy functional may be substituted in the TDGL equations,

$$\frac{\partial\phi}{\partial t} = \Gamma_\phi\nabla^2[r\phi + u\phi^3 - \psi(\alpha_1 + 2\alpha_2\phi) - \kappa_\phi\nabla^2\phi] + \eta_\phi,$$
(7)

$$\frac{\partial\psi}{\partial t} = -\Gamma_\psi[W\psi(\psi - 1)(\psi - \tfrac{1}{2} - \theta) - \phi(\alpha_1 + \alpha_2\phi) - \kappa_\psi\nabla^2\psi] + \eta_\psi,$$
(8)

where η_ϕ and η_ψ represent Langevin-type thermal noises which satisfy the fluctuation dissipation theorem [12]. It is well known that nuclei of the lower free energy phase (i.e., crystals) can be formed only from sufficiently large thermal fluctuations, i.e., only the large fluctuations (i.e., nuclei) can grow because of the high penalty of creating an interface. In the simulation, sizable random thermal noise is imparted to trigger a nucleation event. This nucleation process is the basis for interfacial genesis. Once an interface is formed, growth occurs in a manner that is controlled by the interface diffusion and the local free energy difference across the interface.

Figure 1 shows the emergence of a target pattern simulated in accordance with (7) and (8) on a square lattice (256×256) using a finite difference method for spatial steps and an explicit method for temporal steps with a no-flux boundary condition. The concentric rings in the target pattern, analogous to the extinction rings of polyethylene spherulites, are discernible in both the compositional and orientational crystal ordering fields. The classical interpretation of the extinction bands in spherulites is due to the twisting of lamellae (ribbons),

Upper Row - Compositional Order Parameter

200   1,000   2,000   4,000

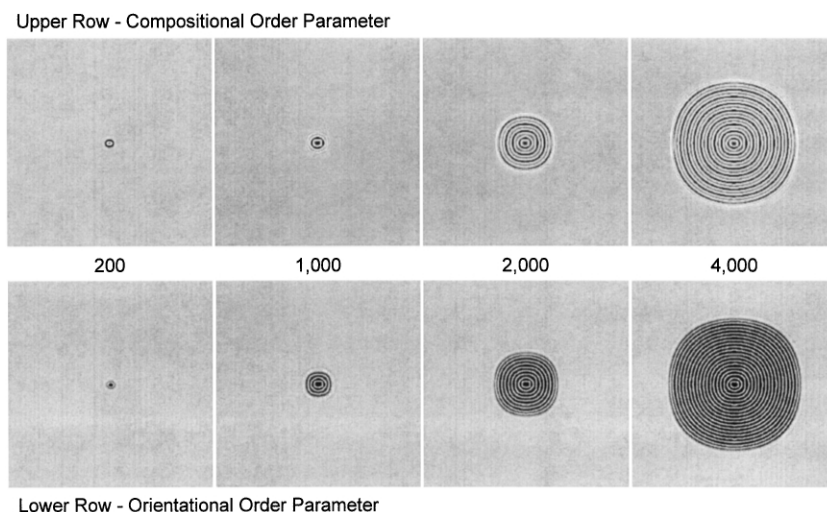Lower Row - Orientational Order Parameter

FIG. 1. Spatiotemporal growth of target patterns generated based on the time-dependent Ginzburg-Landau-equations model C according to (7) and (8). The parameters used in the simulation are $\Gamma_\phi = 0.1$, $r = 1$, $u = 1$, $\kappa_\phi = 1$, $\Gamma_\psi = 1$, $W = 2$, $\theta = -0.3$, $\kappa_\psi = 0.1$, $\alpha_1 = 1$, and $\alpha_2 = 0$.

radiating from a common center (i.e., nuclei) [2]. Keith and Padden [3] argued that the same concentric rings are observable in polyethylene spherulites under the unpolarized configuration; thus, the lamellar twisting orientation cannot be the only cause for the observed concentric ringed patterns in polymer spherulites. They postulated that the concentric ringed pattern is a consequence of structural discontinuities caused by rhythmic crystal growth. The simulated concentric ringed patterns under both the compositional and orientational crystal order parameter fields can reconcile the seemingly opposing view of the lamellar twisting model of Keller [2] and the structural discontinuity model of Keith and Padden [3].

Another interesting feature in polymer crystallization is that a spiral pattern often emerges at the core of some spherulites [2,4]. Recently, we reported a similar observation in blends of polyvinylidene fluoride (PVDF) and polyvinyl acetate (PVAc) under unpolarized microscopic as well as atomic force microscopic (AFM) investigation [5]. As shown in Fig. 2, the simulated spiral spherulitic growth pattern is strickingly similar to that observed experimentally in the 90/10 PVDF/PVAc blends [4]. The observed spiral in the AFM picture indicates that the lamellae are populated more in the ridges than in the valleys, and also appear discontinuous. Again the emergence of spiral patterns is discerned in both the compositional and orientational crystal ordering fields. To the best of our knowledge, the present study is the first to generate the spiral and target patterns from the TDGL model C equations. More importantly, the calculated spiral core remained stationary during growth, which is exactly what has been found experimentally during polymer crystallization [5]. The simulated stationary spiral core is not known in the field of excitable media where the target/spiral corer is constantly pulsating [1], and is thus unique. Our model further predicts that the wavelength of periodic patterns is determined by both the supercooling and the diffusion coefficient through its dependence on molecular weight. However, if the coupling between the two ordering pro-

cesses were weak, the growth occurs via the domain-wall-type propagation, which can be seen in the growth of polypropylene spherulites.

Next, we investigated the growth of PVDF spherulites in the blend with PVAc at various compositions by capturing optical microscope images as a function of time. As depicted in Fig. 3, a stepwise growth was uniquely observed in the plot of the radius of spiral spherulites versus time. At the length scale of lamellar growth, it is well accepted that amorphous chains are rejected from the crystallizing fronts into the interlamellar region. At the larger length scale of spherulitic growth, the noncrystallizing PVDF and amorphous PVAc chains are rejected from the crystallizing ridges (i.e., aggregates of lamellar bundles) into the interspiral valley regions. The increasing concentration of the rejected amorphous PVDF/PVAc chains probably retards the PVDF crystallization; therefore the crystal growth has to slow down. This process is presumably repeated, thereby forming periodic spirals. The same rhythmic growth was also found to occur in the temporal evolution of the concentric rings of PVDF spherulites.

As illustrated in Fig. 4, the rhythmic crystal growth was also captured in the simulation calculated based on (7) and (8) (TDGL model C). This rhythmic growth is characterized by a fast growth followed by a slow growth. It is striking to find that not only the radius increases in a stepwise fashion, but also the total free energy density decreases rhythmically in a synchronized manner (Fig. 4). This finding is seemingly at variance with the general perception that the total free energy density decreases monotonically during crystal growth that occurs via propagation of domain walls. A possible reconciliation is that the present rhythmic energy dissipation is observable specifically in the rhythmic crystal growth. It is noteworthy to mention that the rhythmic growth occurs frequently in nature and it probably shares some common ground with other fields, e.g., the growth of cell population or of land snails [14]. During the
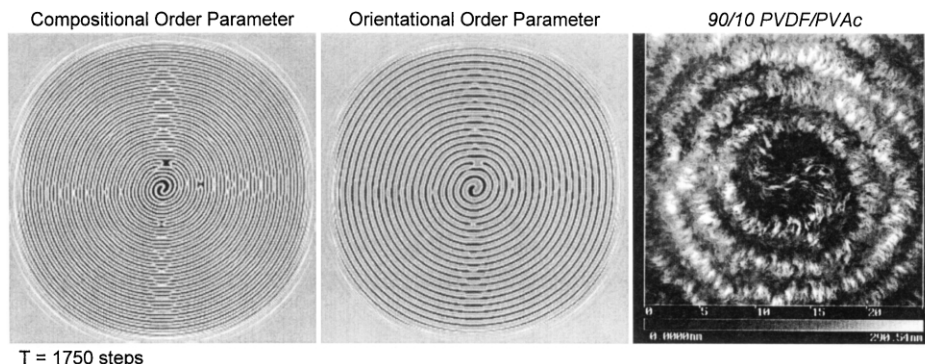

FIG. 2. The calculated spiral growth pattern under the compositional and orientational order parameter fields based on the TDGL model C in comparison with the AFM picture of the 90/10 PVDF/PVAc blend. The parameters for the simulation are $\Gamma_\phi = 0.1$, $r = -2$, $u = 1$, $\kappa_\phi = 1$, $\Gamma_\psi = 0.1$, $W = 1$, $\theta = -0.2$, $\kappa_\psi = 0.1$, $\alpha_1 = 0.5$, and $\alpha_2 = 0.1$.
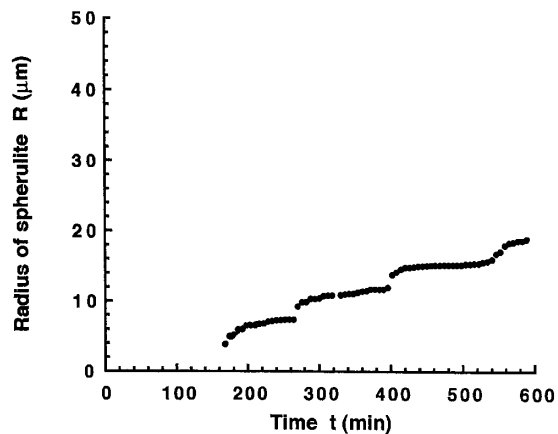
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FIG. 3. Temporal change of radius of spiral spherulite with time showing a stepwise growth for the 70/30 PVDF/PVAc blend at the isothermal crystallization temperature of 167 °C.

course of the revision of the present paper, it came to our attention that the rhythmic radial growth was observed experimentally by Wang *et al.* [15] in ring-banded spherulites of poly(*e*-caprolactone)/poly(styrene-co-acrylonitrile) blends, which further supports our theory.

In summary, on the basis of the TDGL model *C*, the emergence of spiral and target growth patterns in polymer spherulites has been demonstrated theoretically for the first time for a two-dimensional case. Unlike the simulations for chemical waves and physiological systems, the core of the spiral and the target patterns is stationary. An interesting feature is that the periodic concentric rings or spiral texture can be seen in both the compositional and crystal ordering fields. More importantly, the growth of the spiral or concentric ringed PVDF spherulites in the blends with PVAc is found to be rhythmic which can also be confirmed in the simulation. Of particular importance is that the rhythmic energy dissipation occurs with time in synchronism with the stepwise growth of target/spiral spherulites. This finding manifests that the spiral/target spherulitic growth is indeed rhythmic, forming crystalline PVDF rich ridges and amorphous PVAc rich valleys, and thus it is consistent with the structural discontinuity model proposed by Padden and Keith [3] for the polyethylene spherulites. The periodic spiral/target spherulitic structure is presumably superimposed with the twisted lamellar orientation by virtue of the strong compositional and orientational coupling.
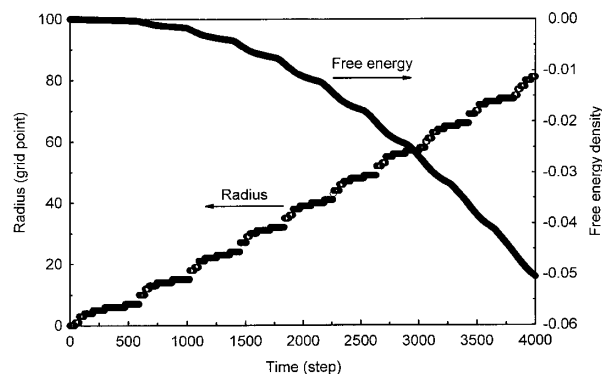

FIG. 4. Temporal change of spherulite size calculated on the basis of the TDGL model *C*, showing the rhythmic growth in synchronism with the rhythmic dissipation of free energy density.

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