String Defects Connecting Pairs of Half-Integer Disclinations and Tilting Transition of a Langmuir Monolayer

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The static and dynamic string defect textures connecting pairs of half-integer disclinations have been observed by Brewster angle microscopy in the solid phase of pentacosadiynoic acid Langmuir monolayers. The static string defect structures have appeared coexisting with two kinds of point disclinations that have four and two black brushes. The use of local laser heating has allowed one to observe kinetics of creation and annihilation of string defects connecting the two-half-integer disclinations in the splitting process of an $s = 1$ point disclination into fractional disclinations. These kinetics have been analyzed by studying the competition between the orientational elasticity of the molecules and the line tension of the string and the drag force of the disclinations.

Introduction

Topological defects, created in symmetry-breaking phase transitions and their dynamical evolution, have attracted much attention in condensed matter physics,[1,2] cosmology, and particle physics[3] because they play significant roles in the formation and stability of mesoscopic- to largest-scale structures. In soft condensed matter physics equilibrium defect textures typically classified as points, lines (strings), and walls have been created depending on the symmetry of the system, and nonequilibrium relaxation dynamics and scaling behavior have been observed in liquid helium,[4] liquid crystals,[5,6] diblock copolymer films,[7] and lipid bilayers.[8] Langmuir monolayers (monomolecular films at the air−water interface) exhibit characteristic textures with distinctive point and line disclinations such as mosaics,[9] boojums,[10,11] stripes,[12] and stars[13,14] in their various mesophases that have quasi-long range orientational order but short-range positional order. There are considerable works, both experimentally and theoretically, on the static properties of these defects and kinetics in phase transitions;[15] however, there is little work on complex string defects and their relaxation dynamics. Only a few examples of such defects have been encountered in other materials. In few-layer-thick freely suspended smectic films, including smectic-*C*, hexatic, and antiferroelectric phases, Pang et al. observed a variety of intriguing two-dimensional (2D) string defects connecting fractionally charged point defects.[16] Rüppel and Sackmann observed two-half-strength disclinations connected by a finite line defect in the λ-$\lambda/2$ symmetry breaking transition of the $P_{\beta'}$ phase of lipid bilayers.[8] They found that the addition of small amounts of impurities, such as cholesterol or protein, effectively leads to the shortening of the line defects that may finally lead to pointlike cores of $s = 1$ disclinations. In Langmuir monolayers, there have not been reports on dynamic line defects, that is, a string defect ending in fractional disclinations. In a previous paper,[17] we reported on the splitting of an $s = 1$ point disclination into two-half-integer disclinations upon laser heating of a pentacosadiynoic acid solid Langmuir monolayer, and we explained this phenomenon from the viewpoint of the energetics of existing disclinations. However, we could not observe the string defects connecting two fractional disclinations. In this paper, we report on the observations of complex textures of both static and dynamic strings (line disclinations) connecting pairs of half-integer disclinations. Local laser heating on the monolayer has enabled one to observe the creation and annihilation of string defects in the splitting process in which two-half-integer disclinations can be created from an $s = 1$ point disclination. The splitting behavior of the two disclinations via the growth of string defects has been analyzed from the viewpoint of their dissipative dynamics.

Experimental Section

Thermomechanical experiments have been performed in monomeric and polymerized 10,12-pentacosadiynoic acid (PCA). Polydiacetylene single crystals, either in bulk or in Langmuir monolayers, have received much attention[18,19−20] because they are model systems for investigating the physics of low-dimensional electrical[21,22] and optical[23,24] phenomena in organic polymers. The well-known fact of this monomer monolayer is that it is polymerized from the solid-state condition topochemically, that is, polymerization may be inhibited if the tails of the molecules in the monomer monolayers are not oriented properly with respect to their neighbors. Here, the focus is switched to the ability of PCA to form $s = 1$ and $s = 1/2$ point disclinations.

PCA was purchased from Wako Pure Chemical Industries, Ltd., and PCA monomers were spread onto pure water (Millipore Milli-Q at 18 MΩ) contained in a home-built Teflon trough. Benzene was chosen as a solvent because larger domains can be obtained with it. A 10 mMol solution of PCA was spread onto the water surface (50 cm^2) until an average molecular area of 23 $Å^2$ was reached. The use of a concentrated solution in a confined small spreading area was crucial for the formation of stripe or point disclination textures.[25] Lower concentrations (for example, ∼0.5−1 mMol) resulted in mosaic textures[26] only. No specific precautions were taken to prevent oxygen-assisted polymerization of the monolayer. Polymerization of PCA was

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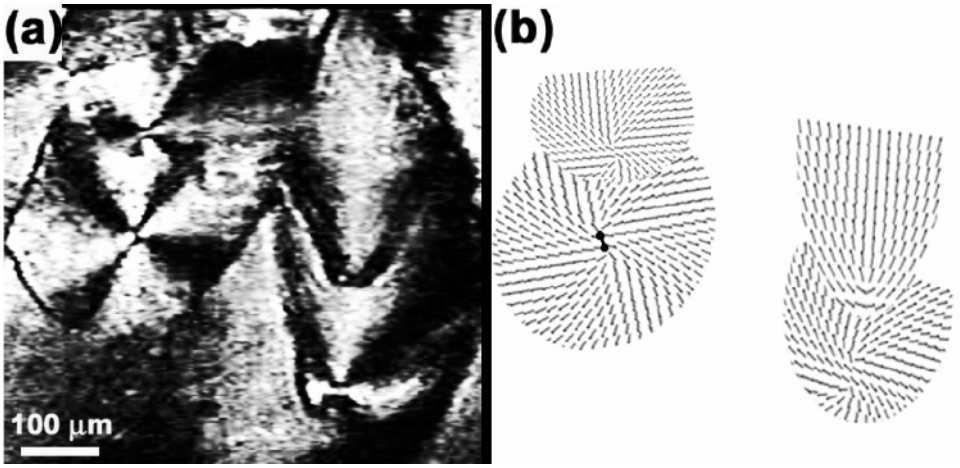

Figure 1. Brewster angle microscope image of a string defect connecting an $s = 1/2$ half-integer disclination at each end coexisting with pairs of $s = 1/2$ disclinations with no strings, in the solid phase of 10,12-pentacosadiynoic acid ($T = 28$ °C, $\pi = 27$ mN/m). Scheme b shows c-director field of the molecules for texture a.

carried out at the water/air interface by exposing the monolayer to a UV-lamp ($\lambda = 254$ nm, 12 W) for 15 min. The distance from the lamp to the monolayer surface was 15 cm.

The Langmuir monolayers were visualized by Brewster angle microscopy (BAM) using an Ar^+ laser. For the laser heating, the monolayer was also exposed to a Nd:YAG IR laser focused on the water surface. A second 20× objective was added to the BAM with the focus arranged so that it coincided with the field of view of the Brewster angle microscope. The power P of the IR laser (after the objective) was adjustable between 50 mW and 2 W. The temperature increase (ΔT) at the center of the hot spot is $\Delta T = \gamma P$ with $\gamma = 10$ K/W. This device has been described in more detail elsewhere.[27]

Results

A string (line disclination) texture connecting two $s = 1/2$ disclinations as well as pairs of $s = 1/2$ disclinations without the strings are shown in Figure 1. For the use of a concentrated solution in a confined small spreading area, the resultant textures and their sizes were sensitive to the subphase temperatures. The $s = 1$ point disclination texture coexisted with mosaic or stripe textures, depending on the temperature. The coexisting mosaics were observed in the range of 0−10 °C, while the stripes were formed in the range of 10−28 °C. We could observe $s = 1$ point disclination textures in the whole temperature range at which we observed, but the number of defects was small at low temperatures (∼0−10 °C), and their size was smaller than when observed above 10 °C. An equilibrium complex of a string with half-integer disclinations at its ends coexists with isolated $s = 1$ and $s = 1/2$ point disclinations at relatively higher temperatures (∼25−28 °C) as shown in Figure 1. The same type of string structure, as observed in this study, where two brushes are linked to each end of the string was observed in smectic-*C* liquid crystals.[16] These structures are metastable in liquid crystals, while our string is stable and does not relax to an $s = 1$ defect. This is consistent with the fact that the monolayer is in an orientationally ordered plastic solid phase.[17] The string defects appear also in a dynamic manner, that is, at the intermediate stage of the splitting process of an $s = 1$ point disclination into two-half-integer disclinations (Figure 2). Local heating ($P = 0.8$ W) forces the $s = 1$ point defect where four black brushes meet at one point ($t = 0$ s) to split into two $s = 1/2$ defects where only two brushes meet at one point ($t = 3.6$ s). During the splitting of the $s = 1$ point disclination, a string defect ending in an $s = 1/2$ defect at each end grows to a finite length of about 10 μm ($t = 1.88$ s), then gradually disappears ($t = 2.04$∼3.6 s). The distance between the two disclinations was not changed substantially in the annihilation process of the string. The time evolution of the separation between a pair of defects is plotted during the growth of the string ($t = 0$∼1.88 s) in Figure 3.

Theory

The dynamics of a string are dominated by a dissipative motion of two-half-integer disclinations that experience (1) the repulsive force f_{elast} that originates from the orientation elastic energy between two disclinations of the half-integer strength, (2) the attractive force f_π due to the line tension of the string that is dependent on the molecular tilt, and (3) the friction force f_d on the moving disclination that results from the entropy production associated with the reorientation process of the molecules that is proportional to the velocity of the splitting disclinations. We assume that the defect velocity is too low to cause flow of the monolayer, that the disclination is of planar type, and that all orientational elastic constants are equal to K. The equation of motion reads

$$f_{elast} - f_\pi - f_d = 0 \tag{1}$$

In a previous paper, we attributed the splitting of the $s = 1$ defect into two $s = 1/2$ defects to a free energy consisting of the sum of the string energy $F_\pi = \lambda d$ (where λ is the string tension and d is the length of the string) of the connecting π-wall, the defect core energy $F_c = 2E_{core,1/2}$, and the elastic energy $F_{elast} = 2\pi K(1/2)^2[2 \ln R/a - \ln d/a]$ (where K is the Frank elastic constant, R is the size of the domain, and a is the defect core radius). If the relaxation of the string length happens by local dissipation, one might anticipate a relaxation that is proportional to the driving force, $f_d = \mu\dot{d}$, that is,

$$\mu\dot{d} = f_d = -\lambda\left[1 - \frac{d_\infty}{d}\right] \tag{2}$$

where $\dot{d}$ denotes the time derivative of d, μ is a friction coefficient, and $d_\infty = K\pi/2\lambda$ is the equilibrium string length. Solving this first-order differential equation, subject to the initial condition $d(t = 0) = 0$, leads to

$$t = -\frac{\mu}{\lambda}\left[d + d_\infty \ln\left|1 - \frac{d}{d_\infty}\right|\right] \tag{3}$$

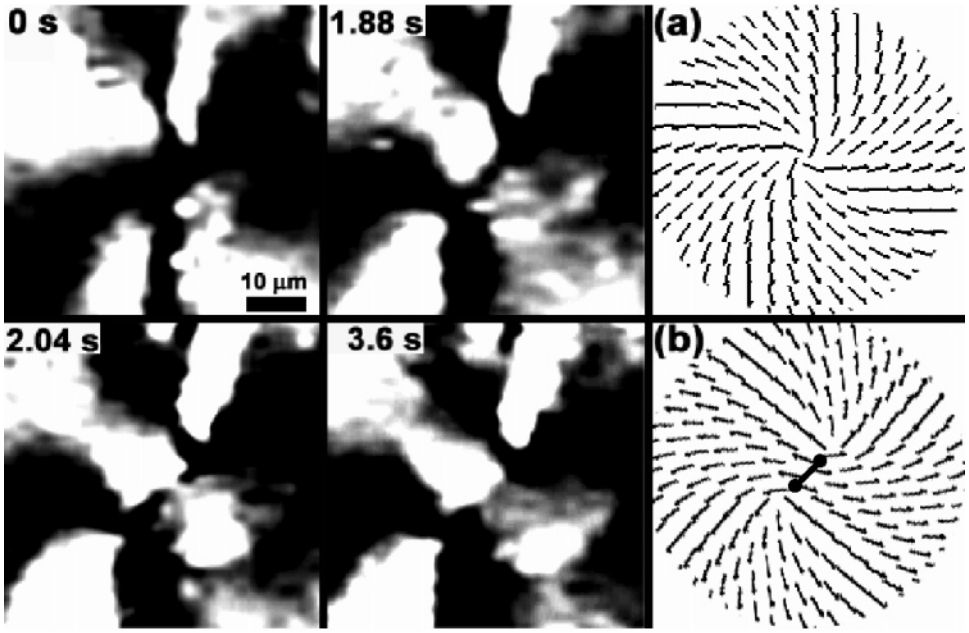

Figure 2. Brewster angle microscope images demonstrating the growth (0−1.88 s) and loss of contrast (2.04−3.6 s) of a string connecting two $s = 1/2$ disclinations in the solid phase of 10,12-pentacosadiynoic acid ($T = 28$ °C, $\pi = 27$ mN/m). Schemes a and b show c-director fields of the molecules in the BAM images ($t = 0$ and 1.88 s, respectively).

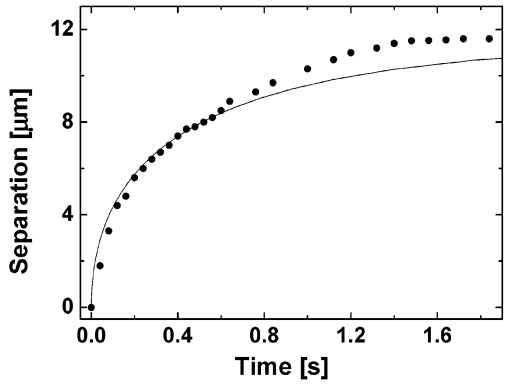

Figure 3. String growth kinetics between two $s = 1/2$ disclinations in the solid phase of 10,12-pentacosadiynoic acid. The solid line represents a theoretical fit with $\mu/\lambda = 0.09$ s/μm and $d_\infty = 11.5$ μm.

describing the relaxation kinetics of the string length. When the tilt θ of the amphiphiles approaches $\pi/2$, the difference between the c-director and its mirror image vanishes. This also means that the π-wall must disappear. In terms of a simple mean field approach, the line tension should vanish as

$$\lambda = \lambda_0 \epsilon^{1/2} \qquad \text{for } \epsilon \rightarrow 0$$

where we have introduced the control parameter

$$\epsilon = 1 - 2\vartheta/\pi$$

measuring the deviation of the tilt angle from $\pi/2$. The parameter ϵ can be thought of as well as $\epsilon = (\sigma - \sigma_c)/\sigma_c$, where σ is the stress created by the laser heating and σ_c is the critical stress required to force the molecules in plane. When we turn on the laser, one suddenly switches from one stress to another and hence there is a sudden jump in d_∞. The texture cannot follow as quickly; thus, the actual length of the string remains unchanged initially and the actual d relaxes according to eq 3 after the switch.

Discussion

The string defect has a finite length and the half-integer strength disclinations are coupled such that the global strength of the complex of defects is integer. The presence of the equilibrium string defect with the macroscopically large core (Figure 1) suggests that the string defects observed here have comparable elastic energy to an $s = 1$ point disclination defects. Generally, two types of point disclinations are observed in nematic schlieren textures: some disclinations have four black brushes, while others have only two black brushes. In smectic schlieren textures, on the other hand, point disclinations always have four black brushes. We could observe both types of disclinations. In this respect, our orientationally ordered solid textures seem to have the characteristics of 2d nematics, from the viewpoint of textures. The half-integer point disclinations are normally forbidden in Langmuir monolayers because of the breaking of the reflection symmetry of the c-director at the air/water interface. The gradual annihilation of the string defect would give direct evidence to the occurrence of the tilting transition upon local heating on the monolayer where the tilt angle of molecules approaches $\pi/2$.[17] We saw that the string, created by local laser heating on the solid monolayer of 10,12-pentacosadiynoic acid, grew with a characteristic time of the order of seconds, which is shorter than those observed in relaxation process of strings or line disclinations of liquid crystals. This result seems to be associated with the comparatively rigid, solid phase in the monolayer. The annihilation of multiple disclinations was observed in the coarsening dynamics of the microdomains of a diblock copolymer film during annealing.[28] The coarsening of the disclination network proceeded under the topological constraint such that a minimum number of dislocations was produced after the annihilation of disclinations. In contrast, in the dynamics of an isolated disclination in our case, such a topological constraint does not work. An $s = 1$ disclination did not split spontaneously into two $s = 1/2$ disclinations unless we put local heating on the texture, however. This indicates that the line tension of the π-wall connecting the two-half-integer disclinations, dependent

on the orientation of the c-director, is the critical factor for us to observe the splitting dynamics of an isolated, integer disclination. The time-dependent string growth could be fitted as the theoretical curve derived above with $\mu/\lambda = 0.09$ s/μm and $d_\infty = 11.5$ μm at the initial growth of the string. The measured time-dependent string length, however, deviates from the theoretical curve at later stages, and it reaches an equilibrium length at a shorter time. It is likely that a refinement of the model taking into account the time-dependent μ/λ will result in a better fit to the measured values. The obtained value of μ/λ ($= 0.09$ s/μm) from the fitting gives a reasonable agreement with μ_{eff}/λ ($=10^{-2}\sim10^{-1}$ s/μm) obtained using a typical line tension λ of about 1−10 pN[29] and an effective friction coefficient associated with the reorientation of the molecules for a moving disclination,[30] $\mu_{\text{eff}} = 1/4\ \pi\gamma s^2 \ln(R/a)$ where the surface rotational viscosity $\gamma = 0.1$ μNs/m,[31] $s = 1/2$, $R = 100$ μm, and $a = 5$ nm.

Conclusions

The growth of a string defect connecting two-half-integer disclinations has successfully been observed in a 10,12-pentacosadiynoic acid Langmuir monolayer by combination of Brewster angle microscopy and local laser heating. The kinetics has been explained by the model, taking into account the orientation energy of the molecules, the line tension of the string, and the dissipation force on the moving disclinations. The origin for the creation of static string defect must be explored.

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