Splitting Fingers under Strain: Pattern Formation of a Dipolar Fluid in a Polymer Medium

S. A. Carter,*,† J. B. Nephew,† and K. Amundson‡

Physics Department, University of California, Santa Cruz, California 95064, and E-Ink, Cambridge, Massachusetts 02138

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We study the formation and evolution of labyrinthine patterns for dipolar fluids inside a polymer medium under mechanical strain. A new general mechanism is proposed to describe the kinetics of the pattern formation that combines orientation ordering and subsequently breaking characteristics of dipolar fluids with branching characteristics of crack-propagation. This mechanism can lead to many of the patterns found in nature, including spots, stripes, labyrinthine, and starlike formations.

Introduction

Generic physical mechanisms acting on a flowable composite media, such as living tissue, can mediate the formation of macroscopic fingering patterns in natural systems.[1] The kinetics for such pattern formation typically falls into two classes, those driven by the interplay of the surface tension and another force, such as the adhesion,[2] density or temperature gradients,[3] and electrostatics,[4] and those driven by reaction−diffusion coupling, such as Turing's model[5] and activator−inhibitor models.[6] In this Letter, we show that for systems consisting of a dipolar fluid dispersed in a polymer matrix another class of fingering patterns occurs that is caused primarily by mechanical strain. The time evolution of the pattern is determined by the branching and eventual breaking of liquid crystalline fingers at areas of high elastic strain within the bulk of the finger. This mechanism can lead to the evolution of a wide range of patterns, from dipolar droplets that coalesce to form channels to fingers that eventually branch to form labyrinthine and triangular formations.

Experimental Section

A dipolar liquid, such as nematic liquid crystals, is known to undergo unusual phase separation dynamics when dispersed inside a reacting medium, such as a monomer under free-radical polymerization.[7,8] In this experiment, liquid crystal and polymer composite films were made from cholorinated hydrocarbon nematic liquid crystals obtained commercially (Merck E7 and TL213) and a monomer consisting of a mixture of 2-ethylhexyl acrylate monomer and trimethylol propane triaacylate cross-linker that resulted in a weakly cross-linked microgel after polymerization. Concentrations between 60% and 80% liquid crystal by volume all resulted in finger formation. The monomer and liquid crystal solution were blended with a dichroic dye, pyrromethane 580 (Exciton), to obtain contrast, and the resulting isotropic mixture was placed by capillary forces into a glass cell with varying gap size 9.5−25 μm. The gap size affected only the diameter of the final channels and the periodicity of the undulations. The monomer was then photopolymerized under a UV lamp, 360 nm at 16 mW/cm^2 intensity, for 5 min so that the polymer was fully reacted. Initial morphologies consisted of small liquid crystal domains, 0.2−3 μm in diameter, dispersed in a continuous polymer matrix.[8] The liquid crystal channels (or fingers) formed 5−30 min after UV exposure with the pattern progressing continuously over weeks as the liquid crystals continued to diffuse into the channels. Images were taken with a low-light high-resolution digital camera (Xillex Microimager-12) and a white light fluorescent confocal microscope (Nikon with Technical Instrument confocal attachment) with 10×, 40×, and 100× oil emersion lenses yielding a maximum resolution of 200 nm horizontal and 400 nm vertical.

Results and Discussion

When the polymer is the minority phase, polymer liquid crystal composite systems typically exhibit a reverse morphology to the standard oil-in-water experiment as the final morphology consists of the majority phase (the liquid crystal) forming discrete droplets while the minority phase (the polymer) forms a continuous porous matrix. Such a morphology is depicted in the background of Figure 1a. This optical image is taken in reflection mode so that the liquid crystal, normally transparent, appears dark, and the polymer matrix, normally opaque, appears light. This droplet pattern is usually considered to be stable; however, we observe that given sufficient strain and fluidity of the porous matrix that this phase is metastable and the liquid crystal domains will coalesce to form liquid crystal channels (or fingers) to reduce the interface surface energy. The finger formation is strain-induced and is caused by the roughly 10% volume contraction of the monomer upon polymerization within the confined geometry established by the fixed cell gap diameter of the Hele−Shaw cell.[9] We observe very few fingers when the strain is relieved from the system by allowing the cell gap to freely decrease as the polymer contracts during po-

* To whom correspondence should be addressed. E-mail: sacarter@cats.ucsc.edu.
† University of California.
‡ E-Ink.

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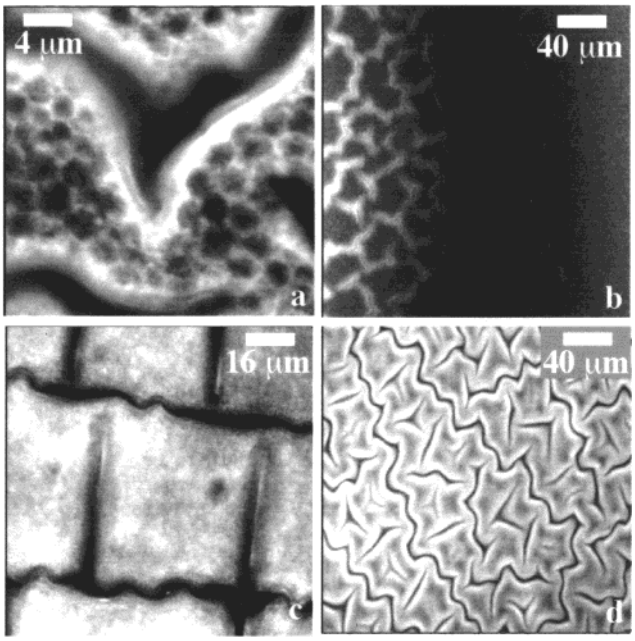

Figure 1. Representative images of the TL213 liquid crystal pattern formation under varying magnification and conditions. (a) The background shows the initial pattern formation of spherical liquid crystal domains dispersed in the polymer matrix. A magnification of a finger tip is shown in the main part of the figure. The slope of the tip indicates the average slope of the liquid crystal anchoring at the surface (see Figure 3). Image is taken in reflection mode with 12-bit camera. (b) On the left side of the cell the liquid crystal/polymer composite is in a confined geometry (glass is anchored) while on the right side of the cell the geometry is open (glass is allowed to float). The labyrinth patterns only form where strain induced from the confined geometry exists. The droplet morphology (unresolved at this magnification) is stable on the right side of the cell. Image is taken in transmission mode. (c) Stripped checkerboard patterns, taken in reflection mode, are often observed. The undulation increases (smaller wavelength) in areas with higher strain. Branching decreases the strain and therefore flattens the undulation. (d) Image, in reflection mode, showing long undulating fingers, side branches, and star formation resulting in a brainlike morphology. The black line down the center of the liquid crystal fingers in panels a and d reflect that the fingers have expanded to a diameter slightly greater than the cell gap so that the liquid crystals at the center of the fingers are now vertically anchored to the cell walls, minimizing reflection.

lymerization, as shown in Figure 1b. Here the optical image is taken at lower magnification and in transmission mode so that the liquid crystal appears white and the polymer dark. The initial size of the channels is resolution limited (<200 nm) and considerably smaller than the cell gap but the channels widen over time to a maximum width set by the cell gap. As is observed in panels c and d of Figure 1, the channels undulate with a wavelength that decreases with increasing strain because of a balance between the energy decrease due the finger's larger area and the elastic energy increase due to its local bending.

Similar liquid crystal undulating channels have been observed in cholesteric liquid crystalline mixtures under electric fields;[10] however, the progression of the fingering patterns observed here appears to be unique, to the best of our knowledge, to dipolar fluids in a polymer medium under mechanical strain. The time evolution of the pattern, shown in Figure 2, is determined by the growing fingers branching off at areas where the curvature of the

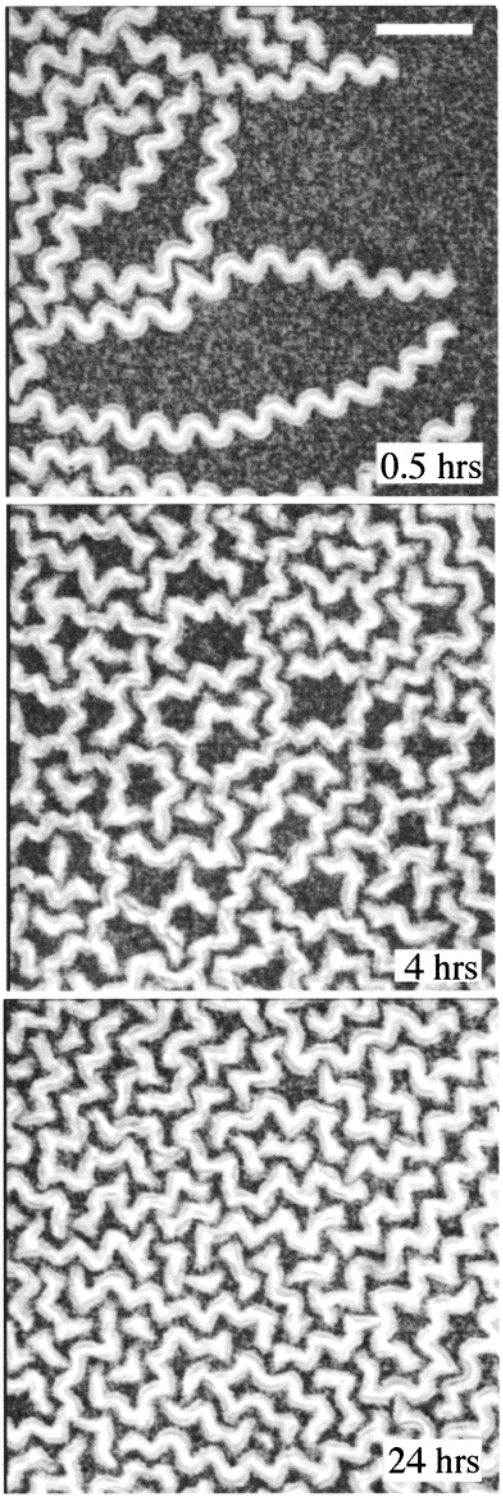

Figure 2. Time evolution of the pattern formation for E7 liquid crystal. The top panel shows the initial formation of long undulating fingers. The middle panel shows a later image when many side branches have formed. The bottom panel shows the space-filling pattern that forms as the fingers break-up into smaller units. Eventually, the pattern will form three-pronged stars, as observed in Figure 1d. All images are taken in transmission mode with a 12-bit camera.

undulation is maximized. This branching forces a labyrinthine pattern to form, Figure 2b, with all three-tiered branches having angles of either 90°, 120°, or 180°, and a subsequent flattening of the undulation. Over longer periods, the fingers physically break at the points of maximum curvature, with the porous media flowing in

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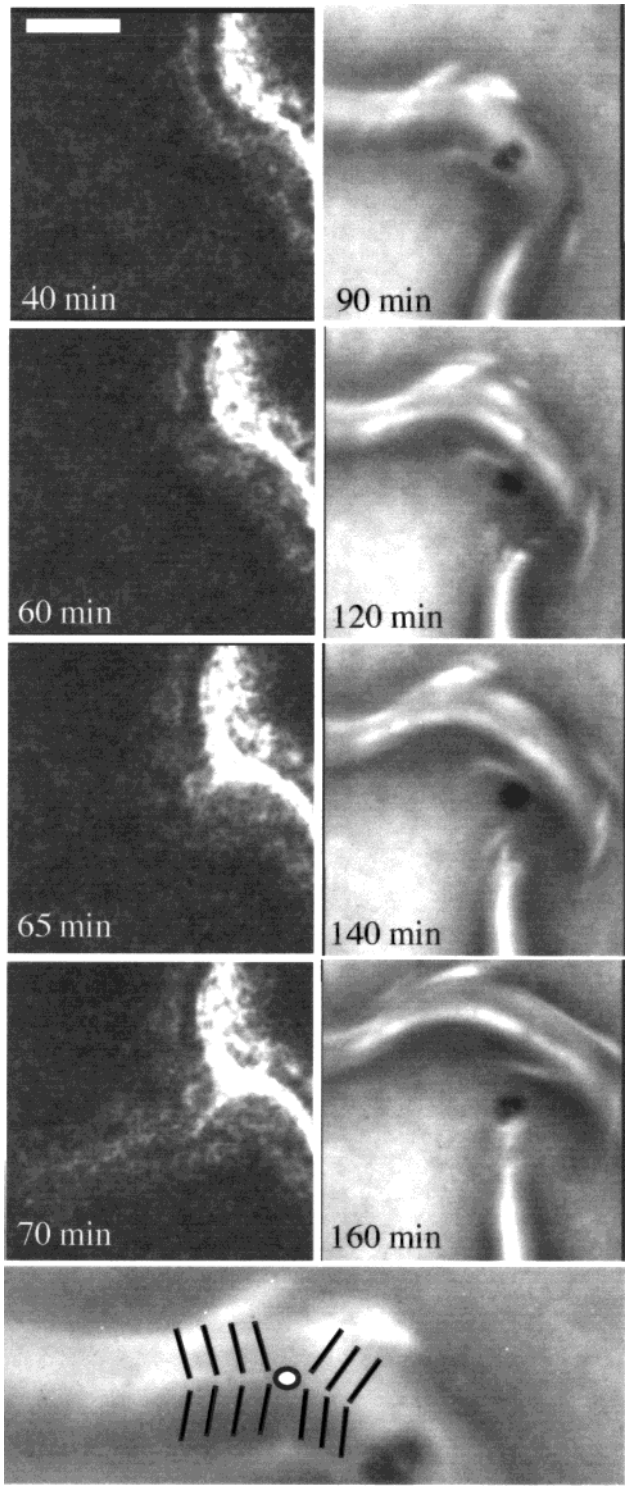

Figure 3. Four frames of movies showing the branching (left side) and breaking (right side) of the liquid crystal fingers. The branching and breaking occur at locations of maximum curvature (elastic strain). (left side) Small branches (diameter ≪ cell gap) which form in the center of the cell will eventually grow to fill the cell gap. Image is taken in transmission mode, 8-bit resolution. (right side) A magnified image of one of the undulations in Figure 2 showing a break forming due to a point defect. The black spot is a location marker for reference. Image is taken in reflection mode, 12-bit resolution. Drawings at bottom of figure show possible liquid crystal surface anchoring and location of point defects.

around the breaks. This results in short branched fingers and finally the formation of three-pronged stars, Figure 1d. Due to the weakly elastic nature of the polymer and the evolution of the liquid crystal fingers, the strain is released over time and the patterns stop evolving.

In Figure 3, we show four frames of "movies" depicting the branching and breaking of the liquid crystal channels. On the left side, the formation of a third branch at the point of maximum elastic strain is observed where the branching provides a method to relieve the local stress, analogous to crack propagation. When the branch first forms, its diameter is considerably smaller than the cell gap. On the right side, a break in the finger is formed at a kink in the undulation, the porous fluid flows in around the break, and the resulting tip continues to grow lengthwise. The branching and breaks are due to the formation of point defects, a characteristic property of dipolar fluid channels. Polarization microscopy on the channels reveals that the liquid crystals are anchored mainly homeotropically (perpendicular) to the surface. The formation of point defects is due to a reversal of the overall orientation of liquid crystals in the finger. A representation of such a point defect is shown in the bottom of Figure 3. As a tip approaches a liquid crystal channel, the liquid crystals in the tip will always be oriented perpendicular to the liquid crystals anchored to the channel surface so that intersection does not occur, as seen clearly in Figure 1c; therefore, the fingers are self-avoiding and require breakage to achieve space-filling structures. We note that although the branching of the dipolar fluid occurs in a porous medium and that fractal-like behavior exists on short time scales, fractal formation is not observed over long time scales since a macroscopic length scale is set by the cell gap.

This system is different than other labyrinthine patterned dipolar fluids[11−13] in that the labyrinthine structures are formed by elastic strain-induced branching rather than by the balancing of interfacial (Young) and electrostatic (Biot-Savart) forces[4] or by the intersection of two progressing fingers.[10] Here, no electromagnetic fields exist to drive the pattern formation nor do the fingers (channels) ever intersect. Also, while the domains are clearly diffusing under strain gradients, no reaction-based diffusion is occurring in this material and the resulting patterns are not consistent with binary fluid phase separation.[14] As such, we have proposed a new general mechanism for labyrinth pattern formation that combines orientation ordering and subsequently breaking characteristics of dipolar fluids with branching characteristics of crack propagation. Such pattern formation should be generally applicable to naturally occurring systems consisting of dipolar fluids confined in a flowable amorphous solid subject to vertical strain, with the time scale for pattern evolution being set by the strain strength and the flowability of the solid medium.

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