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Flow-induced stripe pattern formation in phase-separating fluids

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Abstract

We demonstrated that the introduction of a temperature gradient along the free surface induces a particular stripe pattern in phase-separating fluids. The horizontal temperature gradient drove lateral-periodic spiral liquid motion flowing from warmer to cooler places due to thermocapillarity. Properly chosen polymer compositions and initial film thicknesses in ternary solutions allowed us to promote a phase separation in the presence of spiral flow, which assembled the demixed polymer droplets along the flow-stagnation lines. The resulting assembled phases aligned in the temperature gradient direction and eventually formed periodic polymer stripes involving the same spacing as that of the flow axis. The critical condition for the stripe pattern formation was given by the ratio of two relevant film thicknesses, i.e. the thickness for the onset of the phase separation and that for the cessation of liquid motion.

Keywords: Thin film coating; Phase separation; Thermocapillary convection

1. Introduction

Immiscible polymer blend films commonly exhibit disordered phase morphologies due to their isotropic domain coarsening. An introduction of periodic heterogeneities on interfaces can lead to regular stripe patterns on a micrometer length scale, which is of technological importance for fabricating electronic circuits and other micro-devices. For pre-patterned ‘solid’-film interfaces involving laterally varying chemical end-groups, there have been extensive studies on the surface-induced phase separation [1–3]. The strong affinity of a polymer component to the surface leads to a preferential phase-demixing onto a lower energy surface, resulting in periodic stripes with the same spacing as that of the pre-existing patterns on the surface.

However, the introduction of periodic heterogeneity on an ‘air’–film interface has so far been unexplored. One of the simplest ways to create the heterogeneity is to impose a horizontal temperature gradient along the free surface. The horizontal temperature gradient can drive three-dimensional thermocapillary spiral flows in the liquid when a threshold of instability is exceeded. Theoretical [4,5] and experimental [6–8] studies have demonstrated that the liquid motion showed highly ordered longitudinal rolls with axes parallel to the temperature gradient. When the phase separation takes place in the presence of such an ordered surface flow, we expect that phase-separated domains are self-assembled at warmer stagnation points of the flow, inducing stripe patterns aligned in the temperature gradient direction. Indeed, the surface-tension-driven convection becomes a source of ordered patterns in polymeric liquids [9–11]. Despite the practical utility of ordered polymer patterns, there is little understanding of the coupling between the phase separation and temperature-inhomogeneity on the free surface.

The objective of this article is to show an alternative experimental approach to promote stripe patterns in ternary polymer solutions by introducing temperature heterogeneities on the free surface. This process is in a completely non-equilibrium state, in which unsteady liquid motion influences the phase-separation behavior in the unstable polymeric liquids.

2. Experimental procedure

The polymer blends used in this study contained polystyrene (PS, Wako Chemical, $M_n = 115,000$,

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$M_w/M_n = 1.8$) and polycarbonate (PC, Mitsubishi Chemical, $M_n = 32,400$, $M_w/M_n = 1.8$) where M_n and M_w are the number average and weight average molecular weights, respectively. Both polymers are dissolved in tetrahydrofuran (THF, Wako Chemical, as purchased) as a common solvent. The solvent weight ratio of PS/PC/THF was varied from 1:1:105 to 1:1:51. The experimental apparatus is schematically shown in Fig. 1. The solution was deposited on a glass substrate with a length of 0.10 m and width of 0.025 m. The substrate was mounted on a thermo-sensitive liquid crystal film laminated on an acrylic plate in order to monitor the temperature distributions in the solution. Both edges of the acrylic plate were in contact with two aluminium plates immersed in water baths. The horizontal temperature gradient ranging from 10 to 120 K/m was imposed along the free surface by setting different water temperatures with an accuracy of ±0.1 K. Preliminary monitoring of the air/film interface position indicated that the variation in film thickness was independent of the imposed temperature gradient, showing a negligible contribution of the temperature gradient to the solvent evaporation rate. The polymer solution was dried in the open air to promote the evaporation-induced phase separation. The initial film thickness ranged from 100 to 1000 μm. Top views of the microstructure evolutions in the phase-separating liquid were observed using a CCD microscope (VH-5900, Keyence) and were stored as video images. A toluene etching technique was used to distinguish the polystyrene and polycarbonate phases in the film. The PS-rich phase can be removed by immersion in toluene because toluene is a selective solvent for polystyrene.

3. Results and discussion

Fig. 2 is an example of the photographic sequence showing the stripe pattern formation during the solvent drying. The left and right regions of the figure were heated and cooled, respectively. The initial temperature gradient imposed along the surface was 90 K/m. It was found that an ordered stripe pattern formed on the substrate, aligning in the direction of the temperature gradient. Toluene etching of the dried sample indicated that the opaque stripe-phases were polycarbonate-rich domains, which remained after the immersion of the sample in toluene. The white line in the figure represents the location of the boundary between wet and dried regimes, i.e. the drying front receding from the warmer to cooler places. The magnified image in Fig. 2(b) showed that the same stripes exist in the wet regime as in the dried regime, suggesting that the stripe pattern was promoted by the microstructuring in bulk liquids rather than the interfacial instability [12] of the drying front. The ordered patterns were eventually vitrified in the solid state by the solvent evaporation.

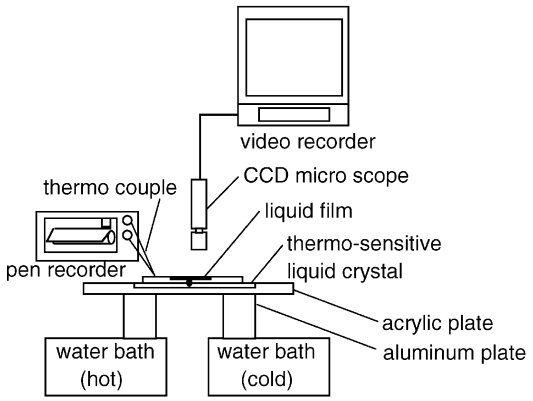

Fig. 1. Experimental set-up. A horizontal temperature gradient ranging from 10 to 120 K/m was imposed in solutions by setting different temperatures in water baths.

The stripe pattern formation was strongly influenced by the evaporative conditions. Figs. 3(a)–(c) show the top views of the final phase morphologies for three different initial film thicknesses. An increase in the initial film thickness resulted in a transition of the phase morphology from a random distribution of distinct droplets (Fig. 3(a)) to periodic stripe patterns along the temperature gradient (Fig. 3(c)). Microscope observations of the top and bottom film surfaces revealed that the periodic stripes developed not only on the top surface but also across the film. At the intermediate thickness of 400 μm, the stripes involved a higher number density than that for the thicker films but exhibited disordered morphologies (Fig. 3(b)).

In the second series of experiments, the imposed temperature gradient was varied, while the initial film thickness was kept constant. The final microstructures at three different horizontal temperature gradients are shown in Figs. 4(a)–(c). With an increase in temperature gradient, distinct phases (Fig. 4(a)) contacted with the neighboring droplets to form assembled polymer phases (Fig. 4(b)). A further increase in temperature gradient eventually leads to the formation of periodic stripe patterns consisting of pairs of droplets (Fig. 4(c)). Figs. 4(b) and (c) revealed that the assembled droplets did not completely coalesce but deformed into a rectangular or hexagonal shape, between which a thin polymer rim remained. The surface profile measurements (not shown) showed that the rim exhibited a convex shape and was situated about 2 μm above the lower surface level of the PC-rich domains, indicating a characteristic feature of polystyrene domain compression due to the packing of droplets.

The ordered stripe pattern formation in Figs. 3(c) and 4(c) can be understood in terms of the coupling between surface-tension-driven flows and the microstructure development via phase separation. Our preliminary visualizations of the evaporating films showed a development of stripe-like convections consisting of pairs of counter-rotating longitudinal rolls. Tracking of a dust-particle motion from the video image revealed that the liquid in the rolls moved from the warm area to cool area in a spiral motion. These facts are consistent with the theoretical analysis [4,5] that

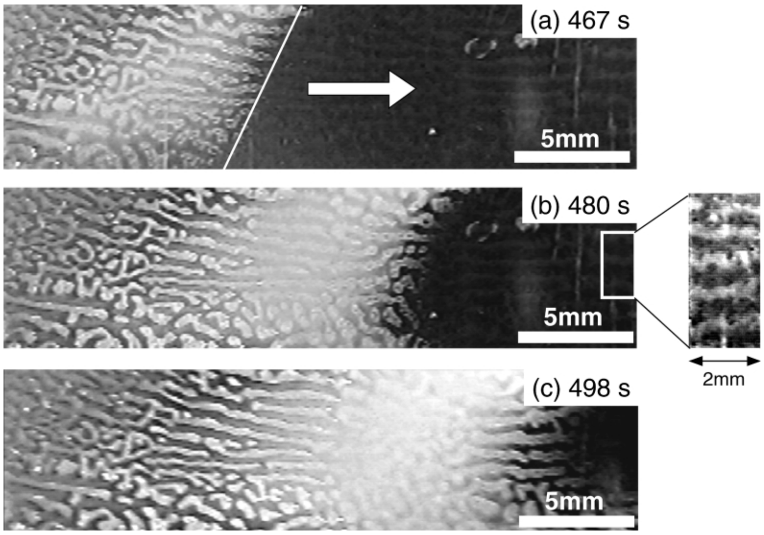

Fig. 2. Photographic sequence of stripe pattern formation. The left and right regions of the figure were heated and cooled, respectively. The white line in the figure represents the location of the drying front receding from the warmer to cooler sites. The polycarbonate-rich opaque phases formed ordered stripe patterns aligning in the direction of temperature gradient. The initial film thickness and temperature gradient imposed along the surface were 800 μm and 90 K/m. Time points indicated in the upper right of each image.

the temperature variation induces a surface tension distribution along the air–film interface, which drives a three-dimensional thermocapillary flow from the lower surface tension region in the warm area to the higher surface tension region in the cool area. When the phase separation takes place in the presence of such a flow, the spiral liquid motion can couple with the phase separation and promote self-assembling of the demixed droplets along the flow-stagnation lines. The assembled phases align in the temperature gradient direction and eventually leave ordered stripe polymer domains as found in Fig. 2.

The coupling behavior between the convection and the phase separation was verified by the transition in the phase morphology from stripes to distinct phases in Figs. 3 and 4. The spiral liquid motion in the evaporating fluids is essentially unsteady. The decrease in film thickness leads to an increase in the conductive heat flux across the film, which dissipates the temperature variations at the free surface and suppresses the spiral liquid motion. The weak convection no longer couples with the phase separation and thus leaves droplet phases in spite of the stripe patterns. This is consistent with the fact that the decrease in film thickness leads to distinct droplet formation in Fig. 3. Similarly, a smaller horizontal temperature gradient promotes fewer stripe phases because of the weaker thermocapillary force. The preferential droplet phase formation in the weak temperature gradient in Fig. 4(a) evidently supports the fore-mentioned physical picture.

Furthermore, the measurements of stripe spacing provided pronounced evidence for the flow-induced pattern formation. Fig. 5(a) shows the measured spacing between the stripes, δ, for different critical film thicknesses for the onset of phase separation. The critical film thickness, h_{ps}, was calculated from the solvent weight fraction at the cloud point, which is depicted in the phase diagram in Fig. 5(b). It was found that the stripe spacing in polymer solutions linearly increases with increasing film thickness. Previous linear stability analysis of spiral flows [5] has demonstrated that the spacing between the longitudinal roll axes is a linear increasing function of film thickness at given fluid

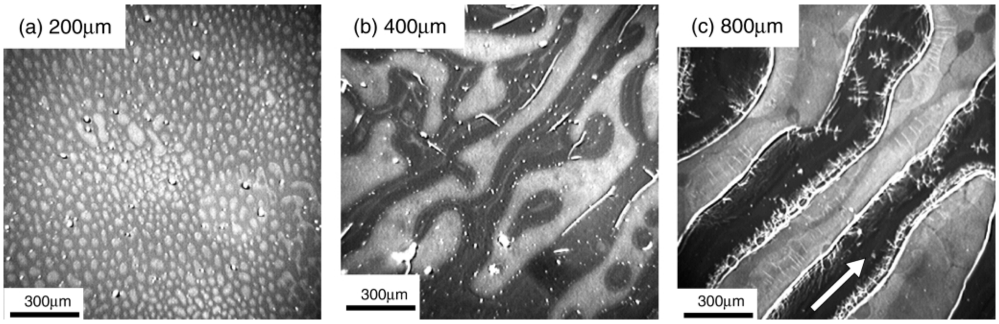

Fig. 3. Variation in phase morphology with increasing initial film thickness. The initial film thickness ranged from (a) 200 μm, (b) 400 μm, (c) 800 μm. The imposed temperature gradient was 100 K/m. The increase in film thickness leads to the transition of the phase morphology from a random distribution of distinct droplets to periodic stripe patterns. The direction of temperature gradient is shown as the arrow in the figure.

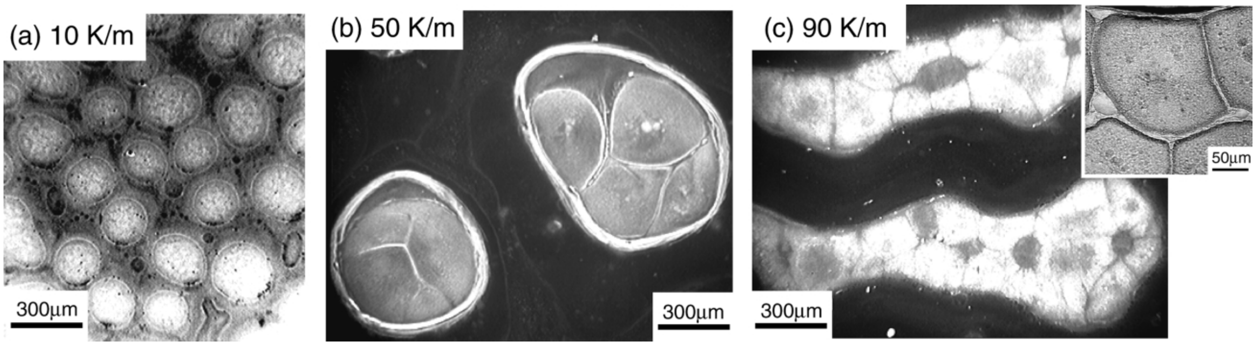

Fig. 4. Variation in phase morphology with increasing horizontal temperature gradient. The temperature gradient ranged from (a) 10 K/m, (b) 50 K/m, (c) 90 K/m. The initial and final film thicknesses were 800 and 15 μm, respectively. With an increase in temperature gradient, distinct phases (a) contacted with the neighboring droplets (b), and eventually formed periodic stripe patterns consisting of pairs of droplets (c).

properties. The closed symbols in the figure represent the measured spacing between the periodic flow axis in the pure solvent [8], showing good agreement with that of the stripe pattern in the polymer solutions. These facts suggest that the phase-separated domains were assembled along the longitudinal roll axes by the spiral liquid motion, leading to involve the same stripe spacing with that between the flow axes. Here it should be noted that the fluid viscosity could alter the spacing between the longitudinal rolls. The hydrodynamic theory [5] showed that the increase in viscosity leads to a wider roll spacing due to the increase in viscous dissipation. Our experiments were limited to the pattern formation at a given fluid viscosity because all the solutions exhibited the same critical concentration, i.e. the same viscosity, at the onset of phase separation.

Recent flow visualization [8] has indicated that the critical condition for the cessation of the spiral flow is denoted by the Marangoni number that expresses the ratio of the surface tension to the viscous force:

$$\mathrm{Ma} = (\partial\sigma/\partial T)(\mathrm{d}T/\mathrm{d}x)h^2/(\alpha\rho\nu) = 0.4 \qquad (1)$$

where σ is the surface tension, T the absolute temperature, $\mathrm{d}T/\mathrm{d}x$ the imposed horizontal temperature gradient, h the film thickness, α the thermal diffusivity, ρ the liquid density and ν the kinematic viscosity of the fluid. To evaluate the effect of the flow transition on the domain assembling, we calculated the critical film thickness for the cessation of the spiral liquid motion, h_c, using Eq. (1) at a given horizontal temperature gradient. In the calculations, the solvent concentration was assumed to be uniform across liquid films, i.e. local variations in physical properties in the thickness direction were neglected. The values of $\partial\sigma/\partial T$ and α were assumed to be the same as those of the pure solvent because the polymer concentration was less than 5 wt% at the onset of the phase-demixing. Because the density ρ and viscosity ν increase during the solvent evaporation, these quantities were measured at the critical solvent concentration, below which the phase separation would occur. Fig. 6 shows the phase-assembling diagram for various temperature gradients and the film thicknesses at the onset of the phase separation. The solid curve in the figure denotes the calculated critical film thickness obtained from Eq. (1). The open and closed symbols represent the regimes in which the stripe patterns (Regime I) and distinct droplets (Regime III) are observed. It was found that the domain assembling into a stripe pattern occurs for specific regions in which the phase separation occurs in films thicker than the critical film thickness for the flow cessation, i.e. $h_{ps}/h_c > 1$. The evaporative conditions in Figs. 3(c) and 4(c) correspond to this region (Regime I). On the contrary, demixed droplets no longer form assembled microstructures for the thickness ratio of $h_{ps}/h_c < 1$, corresponding to the drying conditions in Figs. 3(a) and 4(a). These facts provide conclusive evidence that the phase separation couples with the temperature-heterogeneity-driven flows when the phase-demixing proceeds in the presence of the liquid motion. In

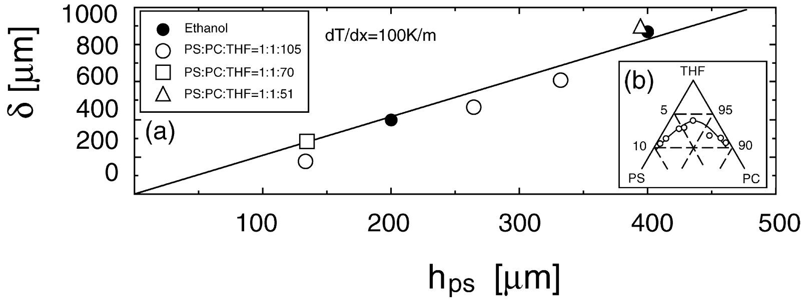

Fig. 5. Effect of film thickness on stripe spacing. The open and closed symbols represent the spacing between stripe domains in the ternary polymer solution and the spacing between the periodic flow axes in the pure solvent. The inset shows the phase diagram obtained from the cloud-point measurements.

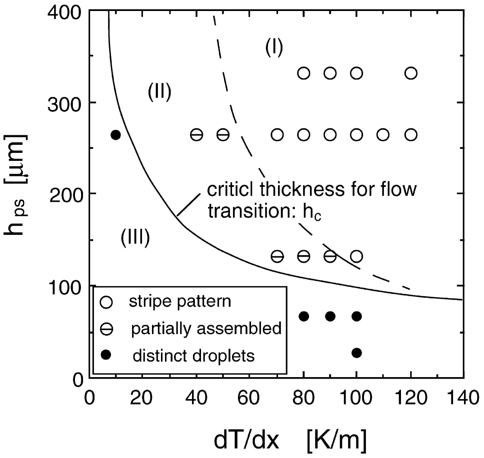

Fig. 6. Critical condition for stripe pattern formation. The solid curve denotes the critical film thickness for the flow cessation. The domain assembling into a stripe pattern occurs for $h_{ps}/h_c > 1$ (Regime I), while distinct droplets were observed for $h_{ps}/h_c < 1$ (Regime III). Partially assembled polymer domains were obtained in the intermediate regime II.

the intermediate regime II, partially assembled polymer domains were obtained (see Fig. 4(b)), suggesting that the spiral liquid motion is too weak to induce a stripe pattern in the range of small temperature gradients.

The results obtained in this study suggest a general strategy for transferring a variation in surface temperature into polymer films. The stripe pattern formation under the influence of surface temperature heterogeneities is schematically depicted in Fig. 7. A horizontal temperature gradient imposed on an evaporating surface first drives regular longitudinal rolls flowing from warmer to cooler places due to thermocapillarity. Properly chosen polymer compositions and initial film thicknesses in ternary solutions allow us to promote a phase separation in the presence of spiral flow, which assembles the demixed droplets along the flow-stagnation lines. The assembled phases align in the temperature gradient direction, deform during their packing process, and eventually form periodic polymer stripes involving the same spacing as that of the roll axis. Since the thermocapillary flow is unsteady, the key is to complete the domain assembling prior to the dissipation of the spiral liquid motion (see Regime I in Fig. 6). The approach presented here can work for a large number of polymer/solvent systems because the temperature-heterogeneity-driven flows can develop in any liquid, once the threshold of instability is exceeded. Furthermore, the present approach can be successfully applied to relatively thick liquid films, in which the interactions between the substrate and polymers are so weak that the preferential self-organization of demixed phases onto a patterned substrate is unexpected.

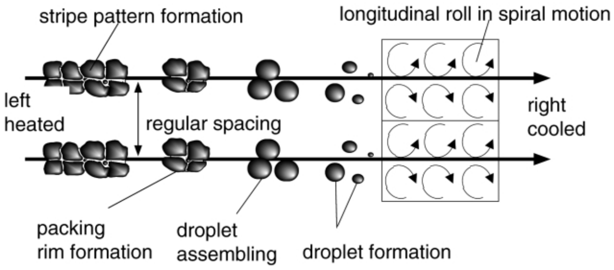

Fig. 7. Schematic diagram of the stripe pattern formation under the influence of horizontal temperature gradient. A temperature gradient drives regular longitudinal rolls flowing from warmer to cooler places due to thermocapillarity. The demixed droplets are assembled by the flow along the stagnation lines and induce ordered stripes involving the same spacing as that of the roll axis.

Although the experimental observations in Figs. 2–6 support the above speculative interpretations, we still have the following fundamental questions: (i) "how does the spiral flow alter the concentration field?" and (ii) "why do polycarbonate-rich phases preferentially assemble along the flow axes even in the nearly symmetric composition?". In the former, the demixing phases possibly experience different shear stresses at different positions in the three-dimensional spiral flow. Such stresses would deform the domain in a complicated manner, which may in turn alter the flow field. For the latter question, the rapid wetting layer formation at the air–film and solid–film interfaces may play a role in the phase demixing. Tanaka [13] has demonstrated that, once the wetting layers form by a hydrodynamic process, the coarsening domains between the layers start to bridge the upper and lower wetting layers and form disc-like droplets with a diameter comparable to the thickness. As found in Fig. 4(a), the diameter of PC-rich droplets in Regime III was 200–300 μm, which was comparable to the thickness for the onset of phase separation of $h_{ps} = 265$ μm. In addition, the diameters of the PC-droplets were one order of magnitude larger than the dried film thickness, exhibiting a particular disc-like shape. A comparison between Figs. 3(a) and 4(a) revealed that the diameter of the PC droplets decreases with decreasing film thickness, showing a qualitative agreement with Tanaka's theory. These facts imply that the polycarbonate-rich phases first wet the air–film and solid–film interfaces and then bridge the layers to form the disc-shaped droplets. However, no direct information is currently available for describing the wetting layer formation in the spiral liquid flows. Here we simply point out that the ordered droplet assembling in Fig. 2 could not be explained by such a wetting-induced phase separation. We need further studies to clarify the effect of wetting phenomena on the stripe pattern formation induced by the ordered liquid motion in demixing fluids.

4. Conclusions

We demonstrated that the introduction of a temperature gradient along the free surface induces a particular stripe pattern in phase-separating films. The experimental observations revealed that the heterogeneity of temperature on the evaporating surface drives a particular thermocapillary spiral liquid motion, which assembled the phase-separated domains along the flow stagnation lines. The resulting assembled phases formed stripes consisting of pairs of polymer droplets aligned in the direction of the temperature gradient, exhibiting the same spacing as that of the flow axis. The critical condition for the stripe pattern formation was given by the ratio of two relevant film thicknesses. The thickness for the onset of the phase separation must be thicker than that for the cessation of liquid motion in order to promote phase assembling into the ordered microstructures.

Acknowledgements

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