

## Ordered Morphologies in Polymeric Films Produced by Replication of Convection Patterns

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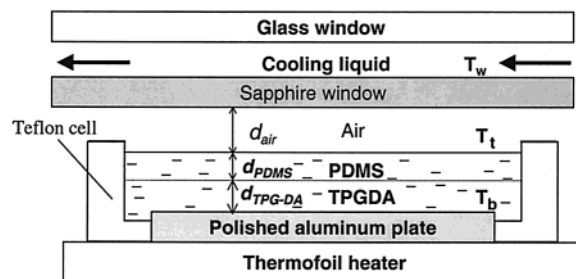
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Recently, self-organization of molecules, colloid particles, and millimeter-size objects in ordered arrays has stimulated great interest in modern materials science.<sup>1</sup> A major challenge is to develop simple and reliable strategies for developing materials with periodically modulated structures. For species that do not self-assemble into the desired structures, a templating approach is beneficial, in which the architecture and the characteristic length scales of the system of interest are determined by those of the template. Here we show a new strategy for producing two-dimensional ordered morphologies in polymeric films, which employs thermal convection in thin binary layers of immiscible fluids. In the first step, periodic nonequilibrium patterns with a high degree of order and symmetry are replicated in a thin layer of a convection-passive monomeric fluid by bringing it in contact with a nonpolymerizable “template” liquid undergoing surface-tension convection.<sup>2</sup> In the second step, the pattern replicated in the monomeric layer is trapped in the solid state by UV-initiated polymerization, and the template fluid was removed. The periodicity of the patterns varies from 0.9 to ca. 2 mm and potentially could be reduced to several micrometers.

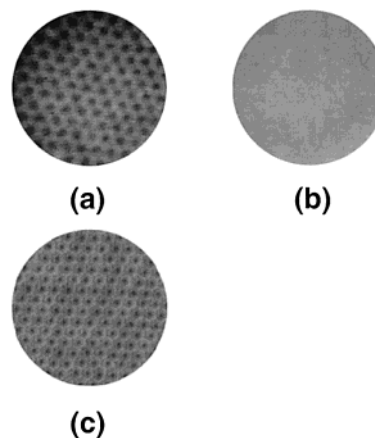
Experiments were carried out in the apparatus previously used for generation and solidification of patterns in single-layer convection-active fluids.<sup>3</sup> Here, poly(dimethylsiloxane) (PDMS) was used as a template fluid, and convection-passive tri(propylene glycol) diacrylate (TPGDA) was employed as a monomeric fluid. A binary fluid layer was subjected to a vertical temperature gradient by heating the bottom and cooling the top of the film, as shown in Figure 1.

The temperature difference,  $\Delta T$ , across the liquid film was induced by increasing  $T_b$  in steps of 0.2 °C, while keeping  $T_t$  constant. The nonequilibrium structures generated in the fluid film were visualized using a shadowgraph technique and a CCD camera Pulnux TM 40 linked with a computer-controlled frame grabber and a time-lapse VCR. When a desired ordered convection pattern was induced in the monomeric fluid, the binary layer was illuminated with the UV light for 3 min to trap the patterns in the solid state.

Prior to experiments with the binary liquid films, convection was studied in the single layers of PDMS and TPGDA. Figure 2a shows a hexagonal pattern typical for the surface-tension-driven convection generated in the PDMS layer for  $\epsilon = 1.73$ , where  $\epsilon = (\Delta T - \Delta T_c)/\Delta T_c$  and  $\Delta T_c$  is the mean temperature difference across the layer corresponding to the onset of convection,  $\Delta T_c = 1.40$  °C.<sup>4</sup> For TPGDA, no evidence of surface tension instability could be resolved up to  $d_{\text{TPGDA}} = 2$  mm and for  $\Delta T$  as high as 22.4 °C (Figure 1b). A similar inertness to Bénard-Marangoni convection was observed in thin layers of other monomeric fluids, presumably due to thermal polymerization in a very thin interfacial layer.<sup>5</sup>

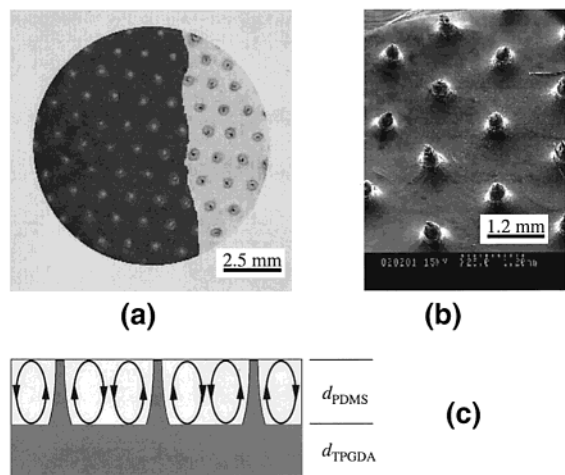


**Figure 1.** Schematics of the experimental setup. The bottom surface of the liquid bilayer has the temperature of the heating plate,  $T_b$ ; the top surface of the bilayer is cooled by purging the cooling liquid at temperature  $T_w$  between the glass and sapphire windows. The temperature difference across the fluid layers was calculated as shown in refs 4 and 6.



**Figure 2.** Convection structures induced in (a) PDMS,  $d_{\text{PDMS}} = 0.65 \pm 0.03$  mm,  $\epsilon = 1.73$ ; (b) TPGDA,  $d_{\text{TPGDA}} = 1.91 \pm 0.03$  mm,  $\Delta T = 22.4$  °C; (c) PDMS–TPGDA bilayer,  $d_{\text{PDMS}} = 0.65 \pm 0.03$  mm,  $d_{\text{TPGDA}} = 0.68 \pm 0.03$  mm,  $\epsilon = 0.22$ . The transition to instability occurs at  $\Delta T_{\text{PDMS}} \approx 1.46$  °C.<sup>6</sup> The images show the shadowgraph snapshot with the diameter of 1.5 cm cropped for better morphology visualization. Bright and dark domains correspond to cold and hot spots, respectively. The dimensionless parameter determining the onset of convection is the Marangoni number,  $Ma = -(\partial\gamma/\partial T)\Delta Td/\nu\rho\kappa$ , where  $\gamma$ ,  $\rho$ ,  $\nu$ , and  $\kappa$  are surface tension, density, kinematic viscosity, and thermal diffusivity of the fluid, respectively, and  $d$  is the thickness of the fluid layer.

Following experiments with the individual liquids, temperature gradient was imposed on the binary fluid film of PDMS and TPGDA. A typical pattern generated in the bilayers is shown in Figure 2c. For  $\Delta T_{\text{PDMS}} = 1.41$  °C, irregular dots emerged in the film, which for  $\Delta T_{\text{PDMS}} > 1.46$  °C transformed into a dark-centered highly ordered hexagonal pattern. The periodicity of the pattern was 1.48 mm, which was close to the characteristic length scale of the planform in the individual PDMS layer subjected to the same temperature gradient.



**Figure 3.** (a) Optical microscopy image of the TPGDA–PDMS film (dark area) and of the polymerized TPGDA film after removing the template PDMS layer (light area); (b) scanning electron microscopy image of the polymerized TPGDA film; (c) schematics of replication of convection patterns in convection-passive fluid.

When the thickness of the template layer was held constant at  $d_{\text{PDMS}} = 0.65$  mm, the variation in thickness of the monomeric layer from ca. 0.5 to 1.6 mm did not notably change the periodicity of the hexagonal pattern. In contrast, for this particular range of  $d_{\text{TPGDA}}$  the variation in  $d_{\text{PDMS}}$  had a strong effect on the convection patterns generated in the binary layer. The planform and the characteristic length scale of the pattern in the monomeric fluid were always determined by the thickness of the template layer. The minimum value of  $d_{\text{PDMS}}$  of  $0.55 \pm 0.04$  mm was determined by the smallest amount of PDMS required to cover the TPGDA layer, while for  $d_{\text{PDMS}} > 2.5$  mm buoyancy-driven convection produced roll-like patterns. Perfectly ordered dark-centered hexagonal arrays with the periodicity varying from ca. 1 to 2 mm were obtained for  $d_{\text{PDMS}} = 0.72 \pm 0.32$  mm and  $86 < Ma < 406$ . For  $Ma < 86$ , no convection patterns were observed in the binary layer; this value of  $Ma$  was close to the theoretical onset of convection at  $Ma_c \approx 80$  predicted by linear theory.<sup>2a</sup>

To replicate the convection planform in the monomeric fluid, it was critical that the two fluids brought in contact had a very limited miscibility. Convection in the binary layer (and in a single PDMS layer) was suppressed when PDMS and TPGDA were maintained in contact for 6 h at 25 °C, because of the partial mutual solubility of the two liquids.

The periodic convection patterns induced in TPGDA were trapped in the solid state by irradiating the bilayer fluid film with the desired convection pattern with UV light for 3 min. Prior to these experiments, photoinitiator, hydroxycyclohexyl phenyl ketone, was dissolved in TPGDA to the concentration 1.0 wt %, which did not notably change convection in the binary layer. After polymerization, the lower TPGDA layer transformed into a transparent solid film, and the PDMS layer became opaque due to phase separation with a small amount of the dissolved monomer.

The left part of Figure 3a shows the top view of the surface of the binary film following UV-polymerization of TPGDA. A hexagonal array of small white dots corresponds to the dark centers of hexagons shown in Figure 2c. The right part of Figure 3a shows the structure of the polymerized TPGDA film after removing the PDMS layer. A typical topography of this film is shown in Figure 3b. The entire surface of the solid film is covered with the periodic tapered pins formed in the liquid state by the hot monomeric fluid flowing upward through the binary layer (Figure 3c). Since the monomer remained convection-passive in the range of  $d_{\text{TPGDA}}$  and

$\Delta T$  studied, the periodic morphology of the TPGDA film was ascribed to viscous drag of TPGDA driven by convection in the PDMS layer.

The characteristic length scale of the pattern trapped in solid TPGDA film varied from 0.9 to 2.0 mm and was somewhat smaller than the periodicity of the corresponding convection pattern because of the shrinking of TPGDA during polymerization. The height of the pins on the surface of the polymerized TPGDA film was  $0.80 \pm 0.02$  mm. For the surface tension  $\gamma_{\text{PDMS-air}} = 20.6$  dyn/cm, interfacial tension between PDMS and TPGDA  $\gamma_{\text{PDMS-TPGDA}} = 1.34$  dyn/cm,  $d_{\text{PDMS}} = 0.60$  mm, densities  $\rho_{\text{PDMS}} = 0.93$  g/cm<sup>3</sup>,  $\rho_{\text{TPGDA}} = 1.03$  g/cm<sup>3</sup>, viscosities  $\eta_{\text{PDMS}} = 6.5$  cP,  $\eta_{\text{TPGDA}} = 14$  cP, periodicity of the pattern ca. 1.5 mm, and the interfacial deflection of the PDMS–air interface  $20 \mu\text{m}$ ,<sup>3</sup> the height of the pins was close to the anticipated interfacial deflection predicted by theory.<sup>8</sup>

Several other structures including rolls and squares were trapped in the polymerized TPGDA films, when the thickness of the PDMS layer exceeded ca. 3 mm.

Patterns with a high degree of order and symmetry were trapped in other polymeric films by polymerizing methacryloxypropyl-dimethylsiloxane, poly(propylene glycol) diacrylate, and 1,6-hexanediol diacrylate brought in contact with the PDMS convection template.

In summary, we propose a new approach to producing periodic morphologies in polymeric films. The variation in density, viscosity, thermal expansion, surface, and interfacial tension of the two fluids can lead to principally new morphologies in the films. The monomers can be replaced with polymeric fluids, in which the desired pattern is trapped kinetically by gelation, crystallization, or solvent evaporation. Various template liquids can be used to control film morphology and the periodicity of the pattern. For example, replication of convection patterns induced in thin layers of rapidly evaporating solvents will reduce the periodicity of the replicated pattern to several micrometers.<sup>11</sup>

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## References

- (1) (a) Cox, J. K.; Eisenberg, A.; Lennox, R. B. *Curr. Opin Colloid Interface Sci.* **1999**, *4*, 52. (b) Vickreva, O.; Kalinina, O.; Kumacheva, E. *Adv. Mater.* **2000**, *12*, 110. (c) Bowden, N.; Terfort, A.; Carbeck, J.; Whitesides, G. M. *Science* **1997**, *276*, 233.
- (2) (a) Pearson, J. R. A. *J. Fluid Mech.* **1958**, *4*, 489. (b) Normand, C.; Pomeau, Y.; Velarde, M. G. *Rev. Mod. Phys.* **1977**, *49*, 581.
- (3) Li, M.; Xu, S.; Kumacheva, E. *Langmuir* **2000**, *16*, 7275. Li, M.; Xu, S.; Kumacheva, E. *Macromolecules* **2000**, *33*, 4972.
- (4) The temperature difference across a single layer fluid film was calculated assuming conductive heat transport as  $\Delta T = (T_b - T_w)/[1 + (d_b k)/(d_a k)]$  where  $d_a$ ,  $d_b$ ,  $k_a$ , and  $k_b$  are thicknesses and thermoconductivities of air and the fluid, respectively.
- (5) Xu, S.; Kumacheva, E., unpublished results.
- (6) The temperature differences across the PDMS layer and the TPGDA layer were calculated as  $\Delta T_{\text{PDMS}} = (T_b - T_w)/[1 + k_{\text{PDMS}} d_{\text{TPGDA}}/(k_{\text{TPGDA}} d_{\text{PDMS}}) + k_{\text{PDMS}} d_{\text{air}}/(k_{\text{air}} d_{\text{PDMS}})]$ ,  $\Delta T_{\text{TPGDA}} = (T_b - T_w)/[1 + k_{\text{TPGDA}} d_{\text{PDMS}}/(k_{\text{PDMS}} d_{\text{TPGDA}}) + k_{\text{TPGDA}} d_{\text{air}}/(k_{\text{air}} d_{\text{TPGDA}})]$ .<sup>9,10</sup>
- (7) Degen, M. M.; Colovas, P. W.; Andereck, C. D. *Phys. Rev. E* **1998**, *57*, 6647.
- (8) Loulergue, J. C.; Manneville, P.; Pomeau, Y. *J. Phys. D: Appl. Phys.* **1981**, *14*, 1967.
- (9) For PDMS ( $dy/dT = -6.9 \times 10^{-2}$  dyn/cm grad,  $\nu = 7$  cS (25 °C),  $\rho = 0.930$  g/cm<sup>3</sup>,  $\kappa = 1.1 \times 10^{-3}$  cm<sup>2</sup>/s,  $k = 1.25 \times 10^4$  erg/(cm s grad)) for TPGDA ( $dy/dT = -5.99 \times 10^{-2}$  dyn/(cm grad);  $\nu = 13.6$  cS (25 °C),  $\rho = 1.030$  g/cm<sup>3</sup>,  $\kappa = 1.2 \times 10^{-3}$  cm<sup>2</sup>/s,  $k = 0.53 \times 10^4$  erg/(cm s grad)).
- (10) Koschmieder, E. L.; Prahl, S. A. *J. Fluid Mech.* **1990**, *215*, 571.
- (11) (a) Widavski, G.; Rawlso, M.; François, B. *Nature* **1994**, *369*, 387. (b) Mitov, Z.; Kumacheva, E. *Phys. Rev. Lett.* **1998**, *81*, 3427. (c) Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. *Science* **2001**, *292*, 79.

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