Communications to the Editor

Highly Organized Macroscopic Pattern Observed on the Free Surface of a Polymer Film Cast from a Solution

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Received April 6, 1992
Revised Manuscript Received July 23, 1992

Introduction. In recent years much attention has been paid to nonlinear pattern formation in dissipative systems far from equilibrium.[1] Pattern formation by Rayleigh–Bénard convection in horizontal layers of fluid heated from below is a well-known phenomenon[2] of the nonlinear pattern formation and is of great interest to study. For fluid with a low viscosity, pattern and pattern formation in the fluid layer, of which temperature is sinusoidally modulated, have been intensively studied both experimentally and theoretically.[3-5] Hexagons and rolls have been observed as convective flow patterns. The convective pattern and its pattern dynamics have been studied also for nematic liquid crystals in electrohydrodynamic convection.[6] As for fluid containing polymers, it was expected that the convective flow patterns were not observable because of high viscosity. However, the convective flow pattern in polymeric systems can be seen. Recently, we reported a two-dimensional undulation pattern, which is similar to hexagons of the Rayleigh-Bénard convection, on a free surface of a polymer film cast from a solution.[7] In this study we present a highly organized macroscopic pattern observed on the free surface of a poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (SBS) film cast from its toluene solution. The pattern looks much different from that previously reported.[7] However, we have attempted to explain the undulation pattern of the free surface of the cast SBS films in terms of hydrodynamic instability.

Experimental Section. The specimen SBS that was received from Japan Synthetic Rubber Co. (Sample Code TR2400) was used. The number-average molecular weight (M_n) and the heterogeneity index for the molecular weight (M_w/M_n) were determined to be 6.31×10^4 and 1.15, respectively, by membrane osmometry and GPC. The microstructure of the polybutadiene blocks of TR2400 was characterized by infrared spectroscopy (Morero method[8]) to be 33, 55, and 12 mol % for cis-1,4, trans-1,4, and 1,2 linkages, respectively.

Preparation of a film from a solution was conducted in a container with which the evaporation speed of the solvent can be roughly controlled until the concentration of a solution reaches ca. 70 wt %.[7] The ca. 5 wt % solution of the SBS in toluene was poured into a Petri dish of 12 cm in diameter. Then the Petri dish was placed on a brass plate kept at 50 °C in the container. For this study, the rate of evaporation of the cast solvent was ca. 4 g/h from the beginning up to 20 h (i.e., up to ca. 22 wt % of polymer concentration). The successive solvent evaporation occurred nonlinearly with time, and solidification of the specimen was completed in a total of ca. 35 h. The as-cast films were 0.5 ± 0.2 mm in thickness. A highly organized two-dimensional undulation pattern was observed on the free surface of the as-cast film. To clearly demonstrate the pattern, a transmitted light image through the as-cast film was printed onto a photograph.

Results and Discussion. Figure 1 shows a typical view of the highly organized two-dimensional undulation pattern on the free surface of the as-cast film. Many rings, curved lines, and dots can be distinctly seen in this photograph. The enlarged views are presented in Figures 2–4. Note that Figures 2–4 do not show time-sliced views during pattern formation. The three views are extracted from the different as-cast films in order to highlight different ranks of pattern organization. As the cast solvent evaporates, the viscosity of the casting solution becomes higher and the solution is eventually vitrified. At the moment of solidification, the undulation pattern is recorded onto the free surface of the as-cast film. Since there may be a spatial distribution of a growth rate of the pattern in such a high viscous casting solution, patterns belonging to the various ranks of organization are actually observed on the free surface of the as-cast film, as presented in Figure 1.

We now describe in detail Figures 2–4. In Figure 2 many dots are observed, of which diameters are in the range from 0.01 to 0.2 mm. The dots corresponded to disklike islands. Two types of organization of dots are also manifested here. One is a linear arrangement of the dots, and another is a clustering of the dots. The former looks like a border and the latter a core of a cellular compartment. The cell contains many individual dots. In Figure 3 another type of organization of the dots is detected. That is a circular arrangement of the dots around the core of the cell. The further organized pattern is presented in Figure 4 where a series of rings can be observed in some cells. These rings compose a concentric texture and never cross each other. It is also interesting to examine the pattern near the border between two adjacent cells. There are some incomplete rings, all of which necessarily meet on the border with the other rings belonging to the adjacent cell. Differential interference-contrast microscopy was conducted to survey the degree of the surface undulation. Although the compartments look like islands or peninsulas, these areas were depressed from a "sea" level. The compartments were located at the levels which are 10–100 μm below the "sea". All the disklike islands were observed on the bottom of the compartments, of which thicknesses were from 0.1 to 4 μm.

Let us briefly discuss the surface undulation in relation to the lamellar microdomain morphology at the free surface. The concentric ring texture is very similar to focal conics seen in liquid crystals with a smectic A phase.[9] This similarity implies surface orientation of lamellar microdomains for the pattern formation. Coulon et al.[10] and Collin et al.[11] have studied a surface-induced orientation of the lamellar microdomains of a block copolymer.

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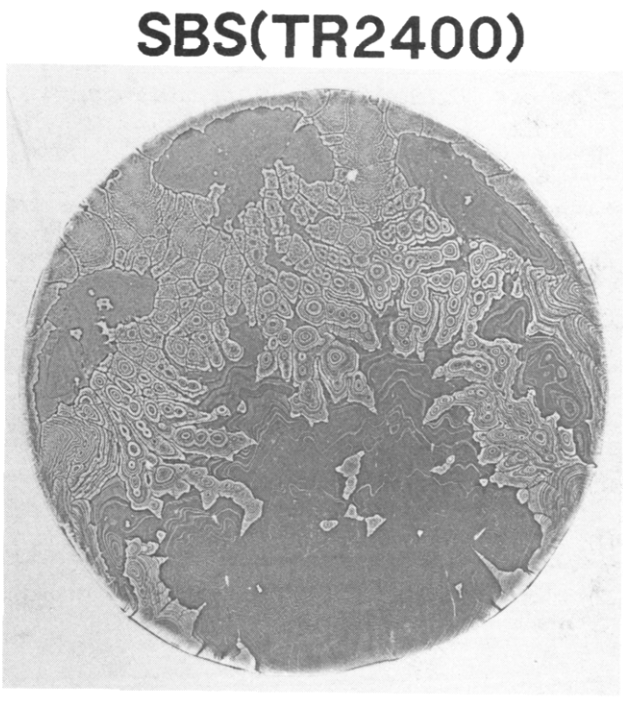

Figure 1. Photograph showing a highly organized undulation pattern on a free surface of the SBS film cast from a toluene solution.

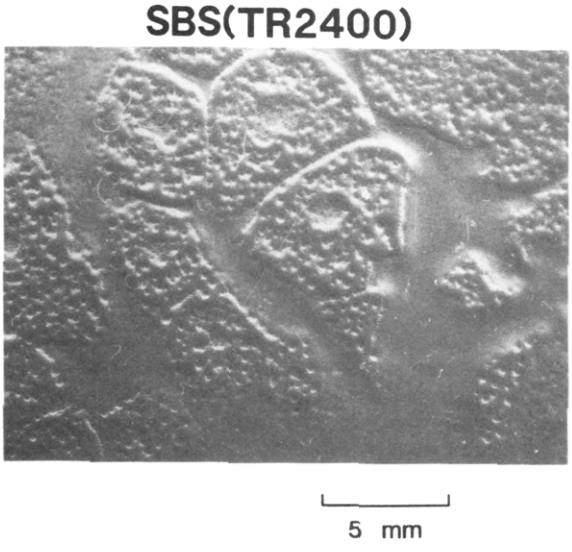

Figure 2. Enlarged view of the surface undulation pattern showing individual disklike islands and an ambiguous cellular organization of the islands.

They reported that the microdomains were aligned primarily parallel to the film surface with an extensive lateral coherence in an annealed thin copolymer film. It was also shown that the surface morphology of the annealed film was governed by the alignment of the microdomains with respect to the surface and the domain periodicity of the alternating lamellae, D. Coulon et al.[10] have found steps near the perimeter of the film specimen by interference microscopy. Collin et al.[11] have reported disklike islands of which thicknesses were roughly identical to D and of which diameters were 0.6–10 μm, as revealed by atomic force microscopy. Contrary to their result, the disklike islands observed in this study have larger diameters and

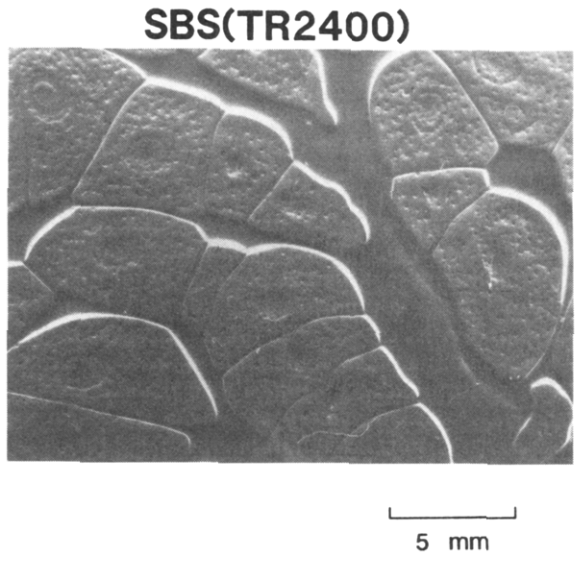

Figure 3. Enlarged view of the surface undulation pattern highlighting a distinct cellular organization of the islands.

Figure 4. *Enlarged view of the surface undulation pattern* highlighting a further organized cellular pattern with a concentric ring texture.

thicknesses. The thickness is 4–160 times as large as a D of 26.6 ± 0.8 nm as analyzed by small-angle X-ray scattering.[12] Though the size of the island is much different from that observed by Collin et al., their results strongly suggest that the surface-induced orientation of the lamellar microdomains may play an important role in the formation of the disklike islands seen in this work. However, another mechanism should be considered for the characteristic macroscopic organization of the islands observed in the cellular compartments. The separate experiments revealed that the pattern formation finished before the solvents completely evaporated. Therefore, it is worth taking hydrodynamic instability into account. We have already reported that the convection was observed in the casting solution with a relatively low polymer concentration.[7] It may be possible to consider that the effect of the convection still remains at the polymer concentration higher than the critical one at which the ordered microdomains are formed. The orientation of the microdomains induced by the convective flows may occur and may result in successive organization of the disklike islands on the free surface. The definite mechanism for the organization is, however, unknown at this stage of the study.

Finally, it should be noted that there are some curved lines instead of the disklike dots in the "sea" area. At the place where these lines exist, the surface undulates. This pattern is clearly different from the cellular pattern and may have a different mechanism of its formation. In conclusion, the surface undulation of the as-cast polymer film displayed a variety of patterns, and it may be very advantageous to study details of the pattern formation triggered by hydrodynamic instability.

Acknowledgment. The authors are grateful to Dr. Q. Tran-Cong at Kyoto Institute of Technology, Kyoto, Japan, for fruitful discussion and generous use of a differential interference-contrast microscope. They thank Professor S. Kohjiya at Kyoto Institute of Technology, Kyoto, Japan, for generous use of a GPC apparatus. They are indebted to Mr. Kenya Makino at Japan Synthetic Rubber Co. for kindly providing the SBS sample (TR2400).

References and Notes

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