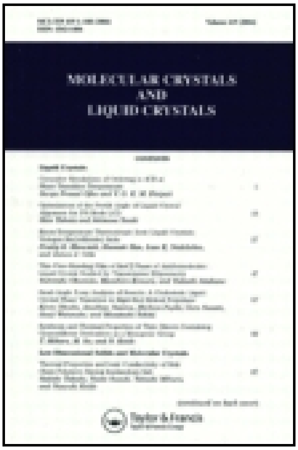

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Photonic and Electronic Applications of Mesoscopic Polymer Assemblies

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Photonic and Electronic Applications of Mesoscopic Polymer Assemblies

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Mesoscopic two-dimensional patterns, regular dots, stripes, and honeycomb networks are formed when dilute organic solutions of polymers are cast on solid surfaces. Dynamic patterns, so-called "dissipative structures", formed in the non-equilibrium thermodynamic process of solvent evaporation, are fixed as the two-dimensional polymer patterns on substrates. Some photonic and electronic applications of the mesoscopic polymer patterns are described in this article.

Keywords: mesoscopic polymer pattern, dissipative structure, dewetting

INTRODUCTION

Great interests are growing in mesoscopic pattern formation based on self-assembling natures of block copolymers, organothiole derivatives and semiconductor materials for micro phase separation[1], mesoscopic surface-patterning (micro contact printing[2]) and quantum-device fabrication[3], respectively, with or without lithographic procedures. Spatiotemporal patterns are generated as dissipative structures under the chemical or physical conditions far from equilibrium. Several types of regular patterns; spirals in the Belousov-Zhabotinsky reaction systems, honeycomb and strips of Rayleigh-Bénard convection, are formed in dissipative processes with various spatial scales from mesoscopic scale of submicrons to macroscopic scale toward kilometer size. Here we report a new general method of the mesoscopic pattern formation of polymer assemblies based on freezing spatiotemporal structures generated in an evaporation process of polymer solutions.

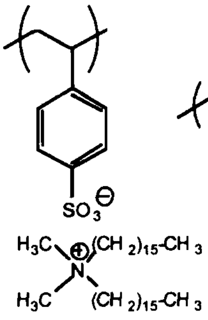
MESOSCOPIC PATTERN FORMATION OF POLYMERS

Due to the evaporation of the solvent, many physical properties, e.g. viscosity, temperature, surface tension, etc. of polymer solutions are dynamically changed during casting process on solid substrates. The casting process is complex enough to form the dissipative structures. If the dissipative structures are formed in the casting solution, some regular patterns of polymer assemblies can be fixed on the solid surface after rapid solvent evaporation.

We have already found that orderly arranged polymer aggregates in submicrometer size were formed when a highly diluted benzene solution of polystyrene was cast on a freshly cleaved mica surface[4]. The diameter of the polymer aggregates is in the range of 300 nm with an average height of 17 nm. The regular pattern is assumed to be formed by synchronization of the fingering instability[5] at the three-phase-line of the casting solution and the dewetting[6] of the hydrophobic polymer from the hydrophilic surface.

Formation of the pattern was followed by *in situ* microscopic observation of a chloroform solution of polyion complexes[7]. Polyion complexes composed of bilayer-forming charged amphiphiles and the counter charged polyelectrolytes, e.g. dihexadecyldimethylammonium bromide and polystyrene sulfonate, **1**, can form ordered two-dimensional layered nano-structures in solvent cast films as well as in Langmuir-Blodgett films[8]. A small amount of a fluorescence probe, octadecylrhodamine B, was added as a counter ion of the polyanion as well as dialkylammonium salts.

As shown in Figure 1 typical dissipative structures are found in the casting process of the polymer solution. The highly diluted chloroform solutions of 1 (a few hundred milligram per litter) was placed on hydrophilic substrates (mica, glass, silicon wafer, etc.) and allowed to evaporate under dry atmosphere. Several numbers of circular domains of Bénard-type convection cells are formed in the central part of the solution.



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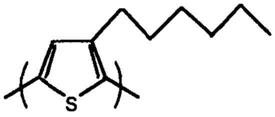

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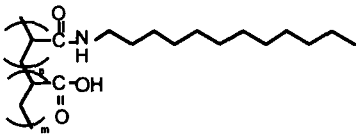

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Radial convectional flows from the center to the solution front are observed, too. Fingering instability is clearly found at the three-phase-line (the solution front) and the fingers are seemed to be connected to the central Bénard cells via the radial convectional streams. The fingering instability can be ascribable to Marangoni effect based on the surface tension gradients at the three-phase-line.

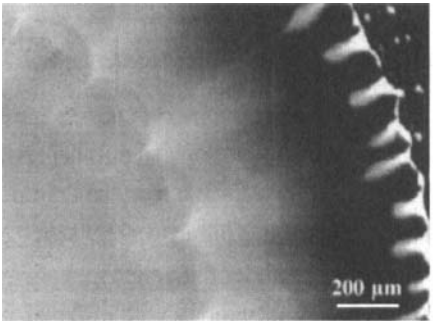

FIGURE 1 Bénard cells and fingering instability in casting solution.

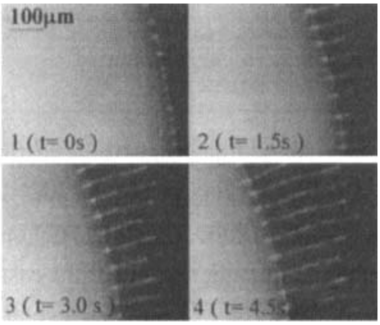

FIGURE 2 Stripe formation from the fingers at the solution front.

Due to evaporation of the solvent, the three-phase-line is starting to recede toward the solution center. When the polymer solution is cast on a smooth surface, e.g. mica, the finger can grow as a line parallel to the receding direction. Figure 2 shows snap shots of stripe formation from the periodically generated fingers. The dimension of the line is several hundred micrometers in length, a few hundred nanometers in width, and several nanometers in height. When the dewetting of polymers occurs in each line, the line ruptures to small polymer droplets. If the polymer dewetting synchronizes with the strip formation, orderly arranged droplets of polymer aggregates are formed as the receding traces.

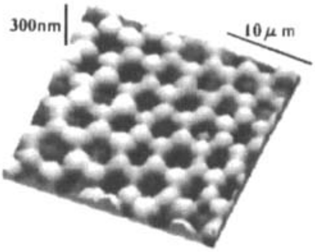

FIGURE 3 AFM image of honeycomb pattern

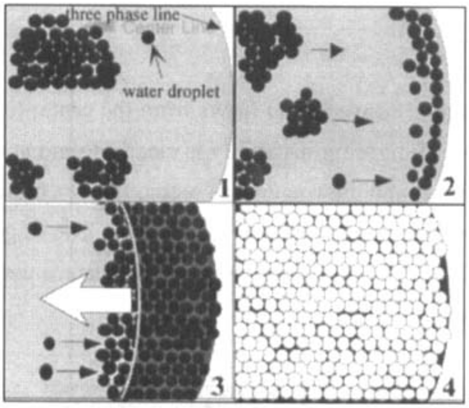

FIGURE 4 Formation mechanism of honeycomb pattern (top view)

At the final stage of the casting, homogeneous and optically transparent polymer films are prepared under dry casting condition. While in the humid casting condition, the film is not optically transparent. Figure 3 shows an atomic force micrograph of the cast film prepared under high atmospheric humidity. The cast film has regular honeycomb morphology with a size of a few micrometers per each cell. From the *in situ* observation of casting process, the formation mechanism of two-dimensional honeycomb is schematically summarized in Figure 4. Due to the evaporation heat of chloroform micron-size water droplets are condensed onto the polymer solution. The hexagonally packed water droplets are transported to the solution front by capillary force and attach to the substrate surface. Since the surface active polyion complex reduces the surface tension between water and chloroform, the water droplets are stabilized against fusional coalescence. Upon evaporation of the solvent the tree-phase-line moves over the hexagonal array of the water droplets. Finally after water evaporation polymers are fixed as the regularly ordered honeycomb pattern on the substrates[9,10].

PHOTONIC AND ELECTRONIC APPLICATION OF MESOSCOPIC POLYMER PATTERNS

Photoconductivity Measurement of Single Molecular Cord of Polythiophene

Conducting polymers (polyhexylthiophene, **2**) can form mesoscopic two-dimensional patterns on solid surfaces by using the simple casting method. Figure 5 shows the mesoscopic stripe pattern of polyhexylthiophene prepared from chloroform. Single line is expected to be a molecular cord because several hundreds of polymer molecules are tied up in a bundle. To measure the photoconductivity of the single bundle one side of the line pattern was contacted with an Ag-paste electrode and another side was contacted with a microelectrode by the help of a micromanipulator. When the line was irradiated with 510~550nm light, photocurrent was generated (Figure 6). The line structure formed by self-organization works as a photoswitching molecular cord.

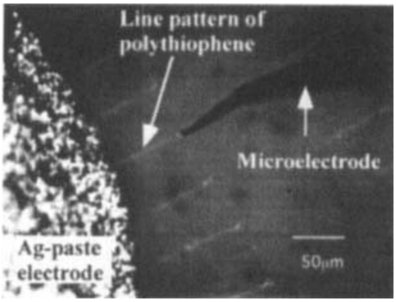

FIGURE 5 Stripe pattern of polythiophene on mica surface

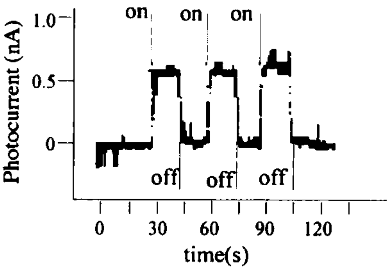

FIGURE 6 Photocurrent of single molecular cord (appl.volt. 10 V)

Preparation of Two-dimensionally Ordered Gold Pattern by Using Mesoscopic Polymer Patterns as Templates

A copolymer of acrylic acid and N-dodecyl acrylamide, **3**, is enough surface active to stabilize water droplets formed on the cast polymer solution. Regularly ordered honeycomb pattern of the polymer **3** was formed on an ITO electrode (Figure 7). After ion coating this structure with a thin gold film, the organic polymer part was dissolved in chloroform and then the substrate was washed by sonication. An optical microscopic observation indicates that the gold film is deposited into the center voids of the honeycomb because the light transmission through the honeycomb pattern in the micrographs turned completely reverse after gold deposition (Fig. 7b).

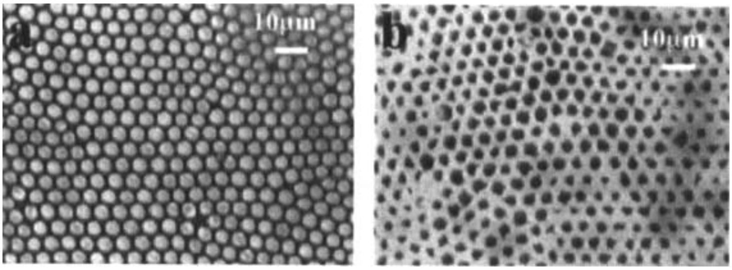

FIGURE 7 Optical micrographs of the polymer honeycomb pattern (a) and gold dot array after removal of polymer matrix (b)

If the polymer is not removed completely, the residual polymer is expected act as an insulating cover layer of the ITO substrate. Figure 8 shows an atomic force image of the polymer-gold hybrid structure after the incomplete removal of the polymer. Electric conduction measured by a modified AFM apparatus, schematically represented in Figure 9, clearly

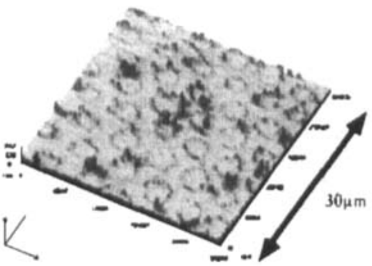

FIGURE 8 AFM image of gold dot pattern in polymer matrix

shows that micrometer-scale conducting gold dots are orderly arrayed in the insulating polymer thin film matrix. By using the self-organized honeycomb pattern of the amphiphilic copolymer as a templates micro patterns of gold dots can be fabricated without photolithography.

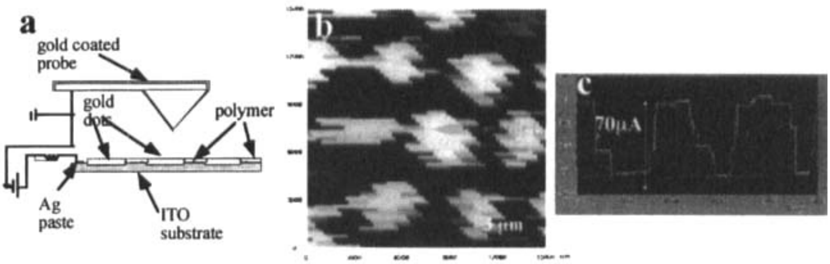

FIGURE 9 Electric conduction measurement of gold dots array in the polymer matrix by AFM. Schematic illustration of conduction measurement (a), mapping of electric current of the polymer-gold hybrid film (b), and cross sectional profile of electric current (c).

CONCLUSION

We have succeeded to fabricate mesoscopic polymer patterns by using self-organization process based on dissipative structures formed in casting solution. We believe that our finding is applicable as a novel general method of mesoscopic structure formation without lithographic processes because the dissipative structures are essentially general physical phenomena for any polymer materials and for any scales from submicrometer to millimeter.

Acknowledgments

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