

**Figure 6.** The sketch in (a) is the cross-section of a typical magnetic microwell template. The cross-section shows the SU-8 layer (light gray) patterned into microwells and aligned over the poles of the micromagnet (dark gray). The optical images (b,c) show two different templates used to direct the assembly of 7.6  $\mu\text{m}$  superparamagnetic beads. The cobalt micromagnets (white) are 20  $\mu\text{m}$  long and 4  $\mu\text{m}$  wide, while 10  $\mu\text{m}$  square microwells approximately 8  $\mu\text{m}$  deep are aligned over the poles of the micromagnet.

using a solenoid coil with an iron core of 2.5 cm diameter. The core was positioned a couple of millimeters away from the substrate in order to provide a substantially uniform magnetic field over the extent of the substrate. This uniform magnetic field was sufficient to bias the magnetic moments of the beads in the direction perpendicular to the substrate. However, the same field had little effect on the magnetization of the micromagnets because of their very high shape anisotropy (extremely large magnetic energy would be required to turn the micromagnets' magnetization out of the plane).

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## Facile Microstructuring of Organic Semiconducting Polymers by the Breath Figure Method: Hexagonally Ordered Bubble Arrays in Rigid-Rod Polymers\*\*

By Lulu Song, Ruta K. Bly, James N. Wilson, Selma Bakbak, Jung O. Park, Mohan Srinivasarao,\* and Uwe H. F. Bunz\*

We report the facile microstructuring of conjugated polymers **1–5** (see Scheme 1) into hexagonally ordered two-dimensional (2D) arrays by evaporative cooling with the subsequent condensation of water droplets onto a dilute solution of polymer in carbon disulfide. This report is the first example in which rigid rod-like polymers are microstructured into inverse hexagonal arrays by the formation, and subsequent crystallization of “breath figures”.<sup>[1,2]</sup>

Micro- and nanostructuring of organic semiconductors is of critical importance in the fabrication of photonic bandgap materials and heterojunction devices, such as photovoltaic cells and thin-film transistors.<sup>[3–5]</sup> A variety of templating methods based on self-assembly have been developed to create structures with micrometer and submicrometer dimensions. These include templating using ordered arrays of colloidal particles,<sup>[6–10]</sup> templating using an emulsion,<sup>[11]</sup> honeycomb structures formed by polymers with rod-coil architecture,<sup>[4,12–14]</sup>

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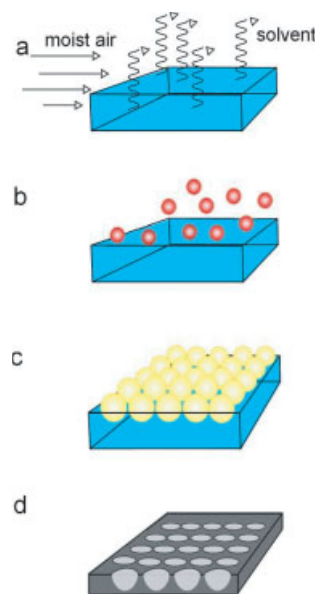
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self-organized surfactants that generate mesoporous silica,<sup>[15–17]</sup> microphase-separated block copolymers,<sup>[18–20]</sup> and even the use of bacteria.<sup>[21]</sup> These templating approaches allow the preparation of macroporous materials that have three-dimensionally (3D) ordered pores with dimensions of tens to thousands of nanometers.

The mesostructuring of organic semiconductors and organic polymers often requires elaborate methods, such as microemulsion processing, template-assisted self-assembly, aggregation of large graphitic hydrocarbon disks,<sup>[22]</sup> and lengthy crystallization methods. With the exception of the Neher–Scherf–Landfester microemulsion method<sup>[3]</sup> that had originally been developed by Stover for non-conjugated polymers,<sup>[23]</sup> and the recent nanotemplating approaches developed by Martin and used by us, there are not many generally applicable methods for the mesostructuring of rigid rods.<sup>[24,25]</sup> This is in stark contrast to the case of block copolymers, where a host of mesostructured systems are easily available by spontaneous self-assembly in the solid state. Particularly spectacular cases include hollow spheres and an example of the “Plumber’s Nightmare”.<sup>[4,26]</sup>

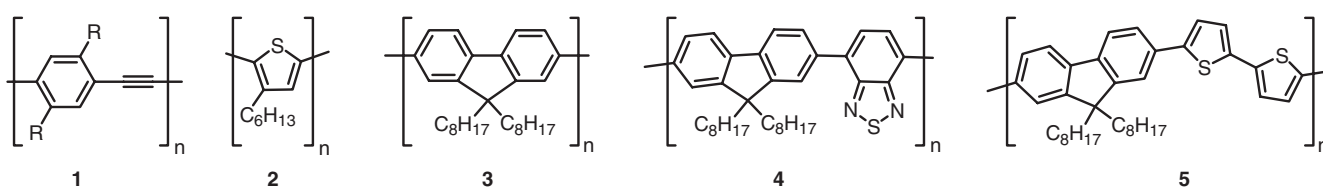
In this paper we demonstrate a simple procedure to create microstructured films of rod-like, conjugated polymers. The experimental procedure consists of taking a dilute solution of a rod-like polymer (**1–5**, see Scheme 1; concentration approx. 0.1–0.5 wt.-%) and evaporating the solvent in a stream of moist airflow across the polymer solution surface. Structures shown in Figures 1–3 develop in a matter of 30–60 seconds. This has been attributed to the formation of breath figures and their subsequent crystallization to develop the ordered array of holes on the polymer film (Fig. 1).<sup>[1,2]</sup> When moist air is in contact with a cold surface (solid or liquid), moisture condenses, forming water droplets that grow with time and form ordered patterns on the surface. Such a pattern formation has been termed “breath figures”. The phenomenon of breath figures has been studied for over a century starting with the early works of Lord Rayleigh,<sup>[2]</sup> Baker,<sup>[27]</sup> and Aitken,<sup>[28]</sup> and more recently by Knobler, Beysens, and co-workers.<sup>[29]</sup> Breath figures form on solids, as well as on hydrophobic liquids, but are only of temporary nature. Should the same experiment be performed upon a solution of carboxylate-terminated polystyrene in carbon disulfide (boiling point 46 °C), then the solvent evaporates and leaves the polymer shells as a nanostructured, highly ordered foam. This method has been used for the nanostructuring of star polystyrene<sup>[30b]</sup> and for rod-coil block copolymers that contain rigid segments such as poly(*para*-phenylene)s or poly(*para*-phenylenevinylene)s. While differ-



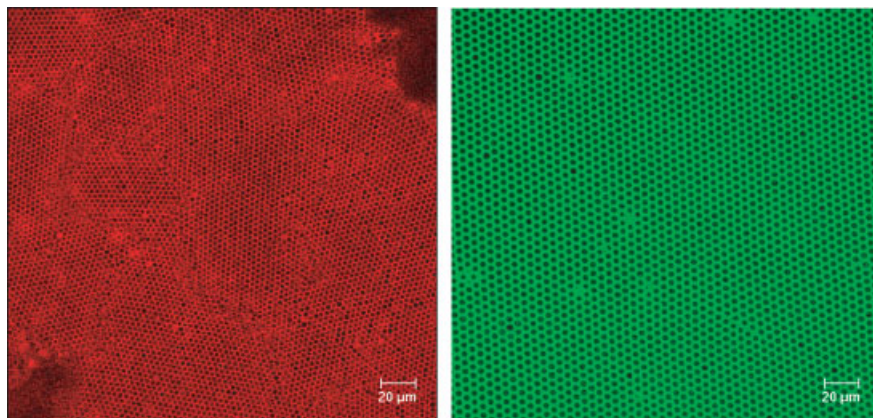
**Figure 1.** Mechanism of bubble array formation utilizing the breath figure method. a) Moist air leads to evaporative cooling of the solvent carbon disulfide. b) Water droplets form by condensation of the warm moist air onto the cold surface of the liquid. c) The water droplets organize into a 2D hexagonal array. d) The water droplets sink into the solution and further evaporation leaves the polymer matrix that has formed by the imprinting of the bubbles as a fossil.

ent polymers have been used with various architectures, they all have a polystyrene backbone or appendage as the structurally unifying feature.<sup>[30]</sup> Bubble array formation is not described in polymers devoid of polystyrene segments in their backbone or in simple rod-like polymers. This lack of data piqued our interest and we investigated polymers **1–5** as substrates for bubble arrays.

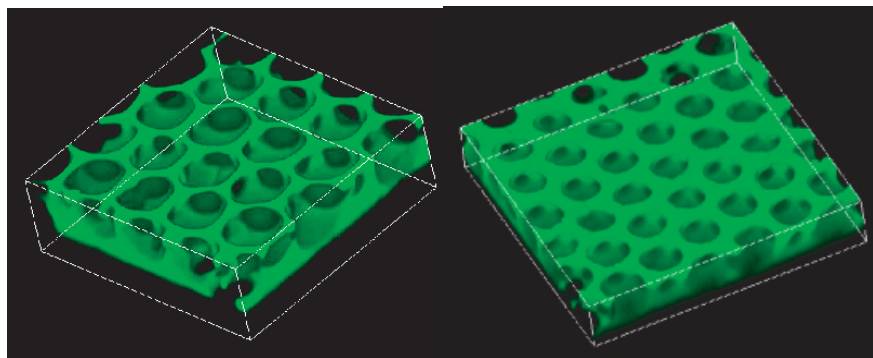
Poly(*para*-phenyleneethynylene) (PPE) **1a** was dissolved in carbon disulfide and a drop of this solution was placed on an untreated glass slide. Evaporation of the solvent in the presence of a moist airflow leads to the structures shown in Figures 2,3. Highly ordered arrays of holes with hexagonal symmetry are formed, with the order extending over a large area (over 1 mm<sup>2</sup>) with almost no grain boundaries. If the experiment was repeated in the absence of moisture in the atmosphere, then one was left with a solid polymer film, devoid of ordered structure. This observation argues for the structure formation being due to “breath figures” and their subsequent crystallization.<sup>[1,2,27–30]</sup> Our model for the formation of the ordered macroporous structures is schematically illustrated in Figure 1.<sup>[1]</sup>



**Scheme 1.** Polymers for bubble formation. Substitution pattern for **1**: a, R = 2-ethylhexyl; b, R = hexoxy; c, R = –CH<sub>2</sub>CH<sub>2</sub>–O–Si(isopropyl)<sub>3</sub>.



**Figure 2.** Hexagonal bubble arrays formed by evaporation of dilute solutions of conjugated polymers in carbon disulfide. Left: Bubble arrays formed from polythiophene **2**. Right, arrays formed from bisethylhexyl-PPE **1a**. The individual bubbles formed by **1a** and **2** are of similar size, but the domain size in **1a** is macroscopic and exceeds 1 mm × 1 mm, while the domain size in polythiophene **2** is 0.05 mm × 0.3 mm.



**Figure 3.** Confocal laser micrographs of monolayers of conjugated polymer matrices containing bubble arrays. Left: Bubbles formed from **1c**. Right: Bubbles formed from **1b**. The bubble arrays formed from **1c** are considerably more durable than those formed from **1b**. The bubble arrays formed from **1b** have thicker walls but are mechanically less stable than the arrays formed from either **1a** or **1b**. The bubbles are 3–5 μm large depending upon the specific conditions of preparation. The box size is 18 μm × 18 μm × 6.2 μm.

Due to the high vapor pressure of the solvent and the velocity of air across the surface, the solvent evaporates, leading to rapid cooling of the surface. Temperatures near 0 °C were measured in our experiments. This cooling leads to the nucleation and growth of water droplets that grow as a function of time.<sup>[1,21,27,29]</sup> The velocity of air, coupled with convection currents on the solution surface that are due to evaporation, drive the ordering and packing of the water droplets. This ordering of holes in the films into hexagonal arrays is not surprising, as it is well known that spheres pack hexagonally on a surface.

Because carbon disulfide is heavier than water, only one layer of the bubbles form. By proper choice of solvents it is possible to form 3D ordered structures.<sup>[1]</sup> A number of factors influence the dimensions of the bubbles;<sup>[1]</sup> however, the primary factor that determines the size of the bubbles is the velocity of airflow across the polymer solution surface. In most

methods of self-assembly the size of the structures are built-in by the choice of the template used. However, in the structure formation reported here, the size of the structure can be dynamically tuned by proper choice of the velocity of airflow across the surface. In Figure 2 micropores formed from bisethylhexyl-PPE **1a** and from poly(hexylthiophene) **2** are shown.<sup>[31,32]</sup> The bubbles are approximately 3–4 μm in diameter and the microstructuring of **1a** occurs over a large macroscopic area, while **2** shows considerably smaller domains of highly ordered bubbles.

In Figure 3 confocal micrographs of two different PPEs **1b** and **1c** are shown.<sup>[33,34]</sup> While both images look similar there is an interesting difference: PPE **1c** forms perfect and durable microstructures, while the dialkoxy-substituted PPE **1b** is mechanically and photochemically much less stable. PPE **1b** forms structures that are not as perfect, mechanically less durable, and display thicker walls. Attempts to utilize a PPE with a more hydrophilic side chain, such as reported by us recently,<sup>[34]</sup> failed. Undefined blobs of air formed under those conditions. The method however works well for polyfluorenes **3** and their heterocyclic copolymers **4** and **5**.<sup>[35]</sup> These polymers give bubble arrays of excellent quality. The degree of polymerization does not seem to be a critical parameter in the formation of the ordered arrays within the experimental range of  $15 < P_n < 300$  repeating units.

In summary, we have reported a simple procedure for microstructuring conjugated, rod-like polymers. The fact that linear rigid-rod polymers form highly ordered arrays of holes under most trivial experimental conditions convincingly refutes the notion that either highly branched or coiled (i.e., polystyrene) structural segments are necessary to generate these arrays. In future we will show that such arrays are useful in directed energy and charge transfer.

## Experimental

The 3D images were obtained using a Leica TCS-SP laser scanning confocal microscope. The sample was excited using the 488 nm line of an Ar<sup>+</sup> laser, and the fluorescence emission was collected using the intrinsic emission of the conjugated polymers. Light emitted from 500 nm to 580 nm was collected to form the images that are shown in the figures. The breath figures were produced utilizing a Caron 5037 airflow-circulator with a Dayton Speed control. The experiments were

conducted with water-saturated air at 25 °C at different airflow speeds. The films were 0.01–0.05 mm thick. Under the fabrication conditions, only a monolayer of bubbles is observed, never bi- or multilayers. Thicker films form from more concentrated solutions and array formation is less reproducible in those cases. Disordered arrays are generally seen. The polymers utilized were made according to the literature [31–36].

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## Solution-based Fabrication of High- $\kappa$ Gate Dielectrics for Next-Generation Metal-Oxide Semiconductor Transistors\*\*

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The semiconductor industry is currently in the process of a transition from 200 mm to 300 mm wafer size and is facing high manufacturing costs and enhanced energy consumption.<sup>[1]</sup> It is believed the associated retooling of processing equipment capable of handling 300 mm wafers and requirements for innovative materials, will become the most expensive in the history of the industry.<sup>[1]</sup> This situation accelerates the development of semiconductor processes that use simpler apparatus and are more flexible, in order to reduce the manufacturing cost to a manageable level. At the same time, down-scaling of the metal-oxide semiconductor (MOS) device to the sub-0.1  $\mu\text{m}$  regime poses serious problems, because conventional SiO<sub>2</sub> gate dielectrics would become thinner than

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