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Two- and Three-Dimensional Crystallization of Polymeric Microspheres by Micromolding in Capillaries**

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Two-dimensional (2-D) arrays of colloidal particles are interesting for potential applications in optical devices, data storage, and microelectronics and as models for protein crystallization.[1–5] Fabrication of these arrays usually involves deposition of a thin layer of a suspension of monodisperse colloids on a flat surface, followed by evaporation of the solvent.[6] The mechanism of the assembly of the particles involves nucleation initiated by capillary forces and growth driven by a laminar flow and evaporation of the solvent.[7,8] The most commonly used system for colloidal assembly has been the fabrication of 2-D arrays of latex microspheres (usually polystyrene); these particles can be synthesized with precise control over sizes from ~ 100 nm to $\sim 100\,\mu$m.

This paper describes the fabrication of crystalline 2-D and quasi 3-D arrays of microspheres, patterned in the plane of the support, using a technique we refer to as MIMIC (micromolding in capillaries)[9] that was developed for the fabrication of polymeric microstructures of organic materials. Using MIMIC, we have fabricated 2-D and 3-D arrays of polystyrene microspheres in enclosed, continuous channels formed by conformal contact between a support and an elastomeric master[10–13] whose surface was patterned with relief regions. This simple procedure has generated patterned, 2-D and 3-D arrays of microspheres on different substrates, and this patterning is what distinguishes this process from previous work.

Figure 1 shows a schematic outline of the process used to crystallize microspheres using MIMIC. An elastomeric mold was fabricated from poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) using procedures for making stamps used in microcontact printing (μCP),[10–13] by casting PDMS against a master that contained a pattern complementary to that to be reproduced. A typical length of the mold was approximately 0.5 to 1.5 cm, and the mold covered approximately 0.5 to 4 cm^2. Both ends of the channels in the mold were cut to allow the fluid to enter and

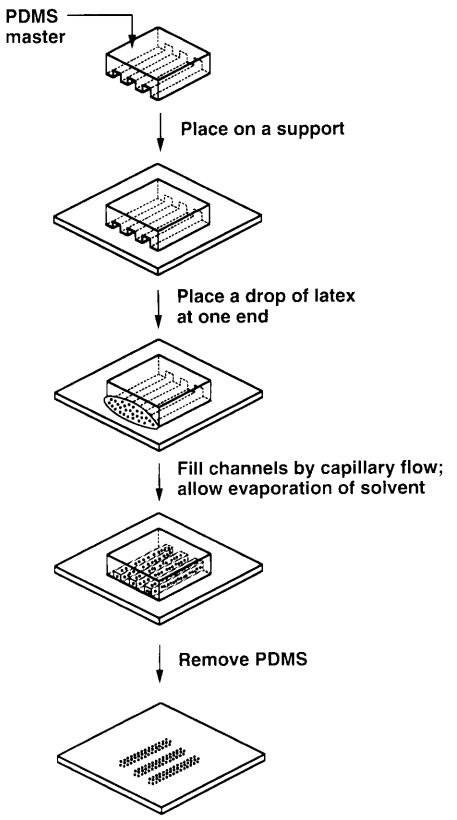

Fig. 1. Schematics of MIMIC in the crystallization of polystyrene microspheres.

air to escape. Opening both ends was essential for this process to be successful.

Prior to MIMIC, the support (glass or Si/SiO_2) was washed with a solution of peroxysulfuric acid (H_2O_2:H_2SO_4 = 1:3 by volume), rinsed with water, and dried with nitrogen. When the mold was placed on the support, the compliant nature of the elastomer allowed conformal contact between the mold and the support, and a network of channels formed. When a drop of a latex solution (Polybeads, Polyscience) containing polystyrene microspheres was placed at one end, the fluid filled the network of the channels by capillary action. A typical rate for filling capillaries with cross-sectional area of 3–6 μm^2 over glass at room temperature was approximately 1–2 cm/min. We usually positioned the elastomeric mold and support in a such way that the capillary filling was not influenced by the force of gravity.[14]

Once the channels were filled completely, the liquid was allowed to evaporate at room temperature, and the microspheres crystallized onto the support within the confinement of the channels: a pattern complementary to that in the elastomeric mold was generated in a structure of crystallized microspheres. Once crystallized completely, the crystals of microspheres were stable and rigid enough that when the elastomeric mold was peeled away from the support, they retained their shape and structural integrity; the surfactants

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present in the latex solution probably contributed to the stability of these structures.

When crystallization was completed, only ~20–40 % of the channels showed crystallinity in which all microspheres were close-packed. In a typical experiment, we patterned approximately 10–40 mm^2 of close-packed arrays of microspheres. The sections of capillaries could be classified into three regions: crystalline, quasi-crystalline, and amorphous. The exit regions of the capillary showed the closest packing, and the entrance regions were disordered. After filling the channels with the latex solution, we employed ultrasonication to aid packing. Ultrasonication improved the yield of crystallized capillaries by ~20 %; even without ultrasonication, however, microspheres could be crystallized using MIMIC.

The rate of evaporation of the liquid had a role in the crystallization of the microspheres, with slow evaporation aiding crystallization. We carried out experiments at room temperature with relative humidity varying from 30 to 75 %, and under these conditions, evaporation of water through the ends (typically with cross-sectional area of 4–12 μm^2) of capillaries seemed to be optimal. When the rate of evaporation of water was increased by increasing the temperature, there was no significant improvement in the extent of crystallization. In fact, when the procedure was carried out at 60 °C, we found no crystallized arrays of microspheres; only non-crystalline arrays formed. When the procedure was carried out at 4 °C, we did not observe better packing in the crystals.

Figure 2a shows a nearly perfectly crystallized region of microspheres (mean diameter = 450 nm), from a section near the exit end of the capillary; it shows well ordered domains of hexagonally packed microspheres. There are, however, some dislocations in the arrays of microspheres. Each layer of the latex microspheres shows hexagonal packing; in contrast, the layer-to-layer packing is tetragonal. This type of tetragonal packing between two consecutive hexagonal layers has also been observed in other geometrically confined systems.[8,15,16] Figure 2b shows one section of the crystallized microspheres and reveals the packing of three hexagonal layers packed tetragonally. When much smaller microspheres (mean diameter = 100 nm) were used, only quasi-crystalline structures were observed (Fig. 2c).

More complex patterns of microspheres can also be crystallized using MIMIC. Figure 2d shows microspheres crystallized in a pattern that contained sharp corners; it shows an almost complete close-packing. Each layer was packed hexagonally; yet, it contained domains occupied by square-packed microspheres. In this particular case, the lack of geometric space may have caused this tetragonal packing. Unlike the packing observed in Figures 2a and 2b, the packing between the two adjacent layers was hexagonal.

Three distinct regions can be observed from one sample of crystallized microspheres. Figure 3 shows such regions: 3a corresponds to a region farthest away from the ordered

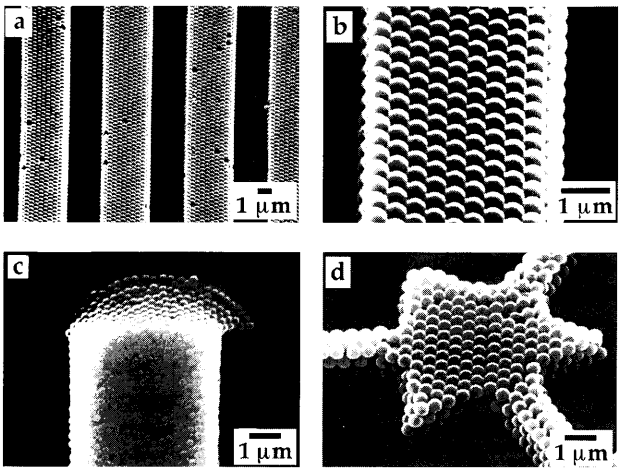

Fig. 2. Electron micrographs of patterned arrays of microspheres. a) Crystallized microspheres (mean diameter 0.45 μm) in rectangular capillaries (4.5 × 1.5 μm). b) A section from (a), showing nearly perfect close-packing. c) Crystallized microspheres (mean diameter 0.10 μm) in rectangular capillaries (3.5 × 1.5 μm). The patterned microspheres are not nearly as crystalline as in (a). The top of the pattern is the exit end of the capillary: that is, the end opposite to that where the latex suspension was supplied. d) Crystallized microspheres (mean diameter 0.45 μm) in capillaries with complex shapes. Note that even sharp corners and edges show good crystallinity.

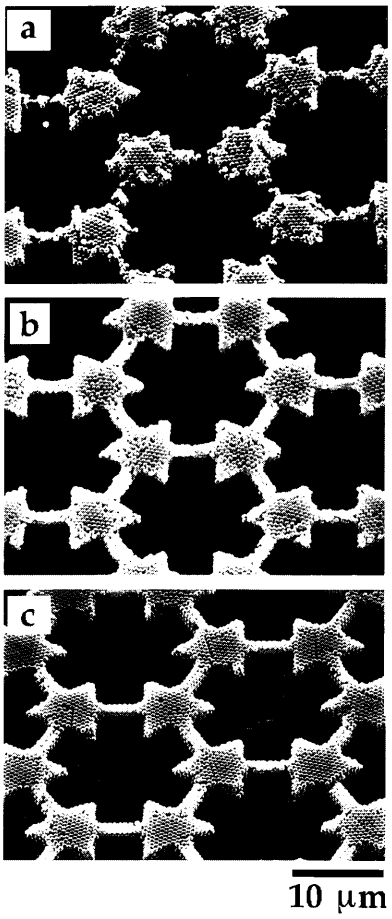

Fig. 3. Electron micrographs showing different stages of crystallization. Pictures were taken from one sample. a) A region where microspheres start to crystallize. b) A region where microspheres have assembled to form the overall shape. c) A region showing complete crystallization.

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ADVANCED MATERIALS

phase of the crystals, 3c a region of the complete crystallization, and 3b a region in between. The crystallization seems to involve three stages: development of nucleation sites, growth of the ordered lattices, and complete crystallization. The crystallization was initiated from nucleation sites (triangular regions) where microspheres had assembled due to attractive capillary forces (Fig. 3a).[7] The growth occurred in "blocks," rather than in layers. We did not observe a complete formation of one layer followed by another; instead, the crystallization occurred in a region where different layers grew simultaneously.

The mechanism we believe to be responsible for transport of microspheres in suspension to the region of ordered lattices is represented schematically in Figure 4. At the exit

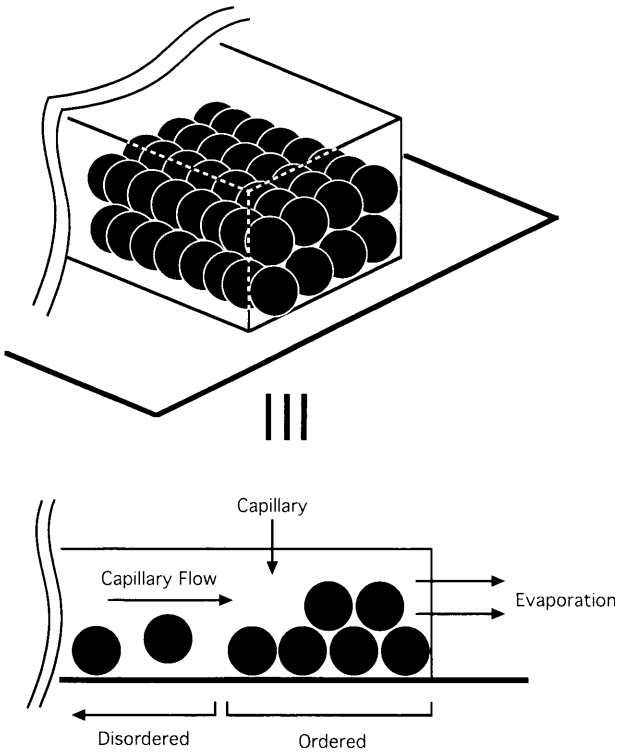

Fig. 4. Crystallization near the end of capillary. Microspheres aggregate near the exit ends due to evaporation and capillary attractive forces. The influx of the latex solution transports the microspheres to the ordered array and the crystallization continues.

end of the channel, evaporation of water and attractive forces between microspheres cause the microspheres to assemble and aggregate into nucleation sites for crystallization. The growth of the ordered lattice is driven by the fluid influx toward the nucleation site in compensation of the water lost by evaporation. This influx causes convective transport of microspheres from the bulk fluid to the lattice, and the growth continues. Because there is a large reservoir of fluid at one end (where the latex suspension is placed), the flux is essentially unidirectional. This proposal of the growth mechanism is consistent with our observations: when the channels were filled from the both ends, no ordered arrays were observed, because unidirectional flow of fluid caused by evaporation did not occur.

MIMIC is a simple, convenient procedure of crystallizing microspheres from latex suspensions onto a support, and it is a method of delivering microspheres to and assembling them in geometrically confined regions on the surface of a substrate. The procedure can fabricate highly ordered 2-D and 3-D arrays of microspheres by self-assembly. The mechanism of crystallization of latex particles in capillaries involves nucleation due to capillary attractive forces between the microspheres and growth due to evaporation and influx of suspension to compensate for the loss of solvent. This process can certainly be extended to particles other than polymeric microspheres, to form highly ordered 2-D and 3-D crystals and may lead to the development of controlled building blocks for well-ordered, patterned monolayers and multilayers of colloidal particles.

This process represents an example of hierarchical self-assembly. The filling of the capillaries is a process of self-assembly templated by the structure of the capillaries; the crystallization of the microspheres is a second self-assembly process occurring on distance scales substantially shorter than the first. The combination of these two processes leads to a structure of a complexity that would be difficult to fabricate by other procedures.

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