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RESEARCH ARTICLE

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Self-Assembly of Pillars Modified with Vapor Deposited Polymer Coatings

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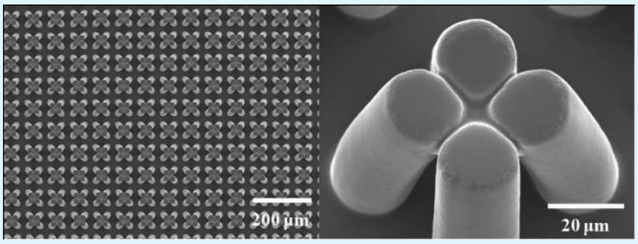

ABSTRACT: In this paper, we demonstrate that thin layers of polymer coatings can be used to self-assemble pillars into stable microstructures. Polymer coatings are deposited onto elastomeric pillars using solventless initiated chemical vapor deposition and capillary forces are used to collapse the coated pillars into microstructures. The location of pillar collapse can be controlled by patterning regions of hydrophilicity and hydrophobicity. Poly(hydroxyethyl methacrylate) and poly(methacrylic acid) coatings stabilize the self-assembled microstructures by providing an adhesive force through solvent bonding. These solvent bonds allow the response of the microstructures to be tuned by varying the thickness of the polymer coating and the solubility parameter of the solvent. The coating process described in this paper is substrate-independent and therefore can be applied to pillars composed of any material.

KEYWORDS: coatings, self-assembly, polymers, capillary forces, soft lithography, adhesion

INTRODUCTION

Nature has demonstrated that interesting surface properties can be achieved by optimizing surface chemistry and surface roughness. For example, the superhydrophobicity of the lotus leaf is achieved through a combination of nanometer and micrometer sized structures on the leaf and a low surface energy wax coating.[1] Microstructured and nanostructured pillars on the feet of geckos enable these lizards to climb up walls.[2] These biological surfaces have inspired researchers to design periodic structures that exhibit self-cleaning[3,4] and adhesive[5−7] properties.

Capillary forces can be used to self-assemble pillars, needles, and nanotubes into arrays of hierarchical structures.[8−13] This self-assembly process is controlled by a competition between elastic forces and capillary forces. The shape and periodicity of the self-assembled structures can be tuned by changing the aspect ratio, spacing, tilt, and elastic modulus of the pillars.[14,15] In most studies, the material used to fabricate the pillars determines both the elastic modulus and the surface energy of the pillars. For example, Yang and co-workers fabricated pillars using different compositions of copolymers and both the elastic modulus and surface energy changed with composition.[16]

In our study, we separate the effect of surface chemistry from the effect of the elastic modulus by using initiated chemical vapor deposition (iCVD) to coat elastomeric poly(dimethylsiloxane) (PDMS) pillars with thin layers of polymer coatings. In the iCVD process, monomer and initiator vapors are introduced into a vacuum chamber where a heated filament array decomposes the initiator into free radicals. The free radicals and monomer molecules adsorb onto the surface of a cooled substrate where polymerization occurs via a free radical chain mechanism.[17−19] The key advantage of using iCVD over liquid-phase processing is there are no solvent tension effects such as wetting or dewetting and therefore the process can be used to uniformly coat nonplanar, curved, and porous substrates. For example, iCVD has been used to deposit uniform fluoropolymer coatings onto electrospun fiber mats[20,21] and membranes.[22]

In this paper, we show that polymer coatings deposited via iCVD can be used to self-assemble PDMS pillars into perfect clusters and light-sensitive coatings can be used to pattern the location of self-assembly. Aizenberg and co-workers recently modified the surfaces of epoxy pillars with short and long chain self-assembled monolayers (SAMs) in order to study the role of adhesion in capillary-forced self-assembly.[23] They found that the chain length and functionality affected the adhesion between the pillars and thereby affected the stability and reversibility of the resulting clusters. Our study confirms their observation that adhesion is important in determining the stability of self-assembled microstructures. However, our method introduces the use of polymer welds, also known as solvent bonds, to stabilize the microstructures. These solvent bonds can be exploited to tune the response of the microstructures to various solvents.

RESULTS AND DISCUSSION

Polymer coatings were deposited onto elastomeric PDMS pillars using iCVD as shown in Figure 1a. The coated pillars were self-assembled using water as the solvent. In order for capillary meniscus forces to collapse the pillars, the water must be able to penetrate between the pillars. As shown in Figure 1b, the uncoated PDMS

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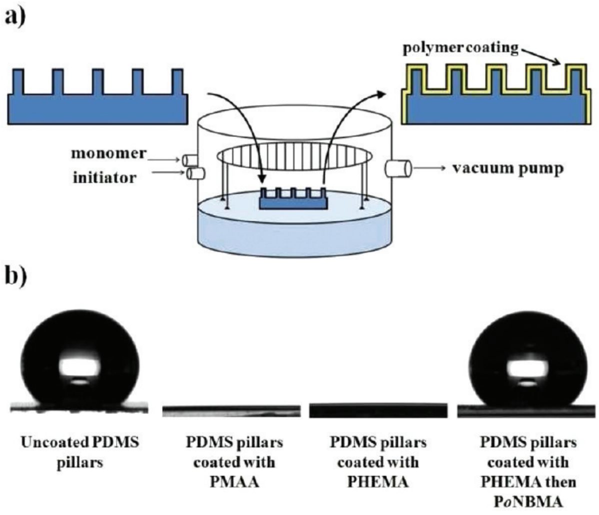

Figure 1. (a) Schematic of the initiated chemical vapor deposition process used to deposit thin layers of polymer onto PDMS pillars. (b) Uncoated PDMS pillars are hydrophobic and water cannot penetrate between the pillars. Water wets pillars coated with PHEMA and PMAA. The hydrophilic pillars can be reverted back to a hydrophobic state by the addition of a thin layer of P*o*NBMA.

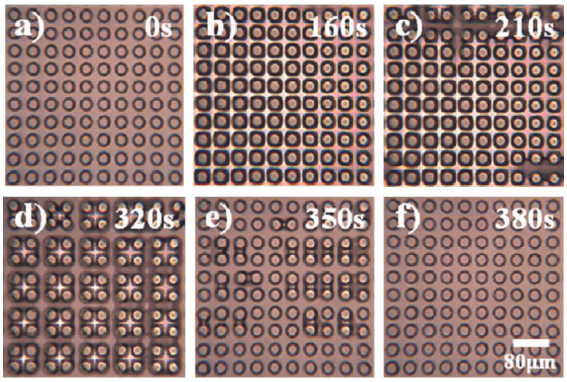

Figure 2. Microscope images of 34 μm tall pillars coated with a layer of PHEMA. (a) Dry pillar array. (b) Pillar array submerged in water. (c) Menisci start to form as water evaporates. (d) The pillars begin to bend into microstructures but do not make physical contact. (e) The pillars begin to restore into their original formation. (f) The pillars are restored to their upright position after complete evaporation.

pillars are hydrophobic therefore water cannot penetrate between the pillars to cause collapse. Deposition of poly(hydroxyethyl methacrylate) (PHEMA) or poly(methacrylic acid) (PMAA) causes the pillars to become hydrophilic and water easily penetrates between the pillars. One distinct advantage of the iCVD process is that different layers of polymer coatings can be stacked onto the pillars without removal of the substrate from the reaction chamber. The hydrophilic pillars can be reverted back to a hydrophobic state by the addition of a thin layer of poly(*ortho*-nitrobenzyl methacrylate) (P*o*NBMA) onto the PHEMA or PMAA layer.

The self-assembly of pillars coated with PHEMA and PMAA was examined by submerging the pillars in water and allowing the water to evaporate. Pillars with a diameter of 22 μm, edge-to-edge spacing of 18 μm, and heights of 34, 54, and 65 μm were tested. The height of the pillars had a large effect on the self-assembly process. In order to collapse the pillars, the capillary force must be greater than the elastic restoring force. The force required to bend a pillar scales as $F \sim Er^4s/h^3$, where E is Young's modulus, r is the radius of the pillar, s is the distance between the pillars, and h is the height of the pillar.[14] If the pillars are below a critical height, the capillary force will not be strong enough to bend the pillars far enough to cause physical contact. Figure 2 shows a time series of the collapse of 34 μm tall pillars coated with a thin layer of PHEMA. Although the pillars begin to bend into microstructures as the water evaporates and menisci form, the capillary force is not strong enough to cause physical contact between the pillars and the pillars are fully restored to their upright position after complete evaporation. When the pillar height is increased to 54 μm, evaporation yields perfect clusters of four pillars (Figure 3). The arrays are defect-free over large areas for both PHEMA and PMAA coatings. At a pillar height of 65 μm, there were several clusters of six pillars in addition to clusters of four pillars.

An adhesive force is required to stabilize the microstructures during self-assembly. Therefore two criteria must be satisfied to form stable clusters: the capillary force must be great enough to cause physical contact and the adhesive force must be strong enough to resist the elastic restoring force. The relationship between pillar height and cluster size has been previously confirmed.[9,16] The novelty of our paper is the demonstration that solvent bonding can be used to provide an adhesive force that overcomes the elastic restoring force thereby enabling the formation of stable clusters. In the absence of adhesive forces, it is expected that the collapsed pillars should revert back to their upright position after complete evaporation and disappearance of the capillary forces. Close-up SEM images of the pillars (Figure 3e,f) show that our pillars remain collapsed after complete evaporation. Visible polymer welds connect the edges of adjacent pillars. These solvent bonds occur when a solvent softens and mobilizes polymer chains and enables them to interdiffuse.[24] These types of solvent bonds are typically exploited to bond polymer pieces composed of the same material together. For example, microfluidic devices can be made by bonding two pieces of poly(methyl methacrylate) together using acetone[25] and ethanol[26] as the solvent. In our system, water is able to soften the PMAA and PHEMA coatings while capillary forces bring the pillars into contact which allows the polymer chains on adjacent pillars to form a solvent bond. For thin coatings, polymer welds are formed between adjacent pillars (Figure 3e), whereas for thick coatings, polymer welds form between the pillars and within the center of the cluster (Figure 3f).

Stabilization by solvent bonding allows us to tailor the response of the self-assembled microstructures to different solvent environments. If the polymer coating is incompatible in the solvent, the pillars will remain collapsed. If the polymer coating is compatible in the solvent, the microstructures will open and revert back to an upright position while submerged in the solvent and then collapse back into a cluster as the solvent evaporates. The amount of cycles of opening and closing depends on the solvent. Because the polymer coating becomes mobile during submersion, bare PDMS can be exposed after repeated use. The cycling can be extended by using organic solvents because of their ability to wet PDMS.

The time required for the microstructures to revert back to an upright position can be tuned by blending solvents. As shown in Table 1, the opening time of the pillars can be controlled by

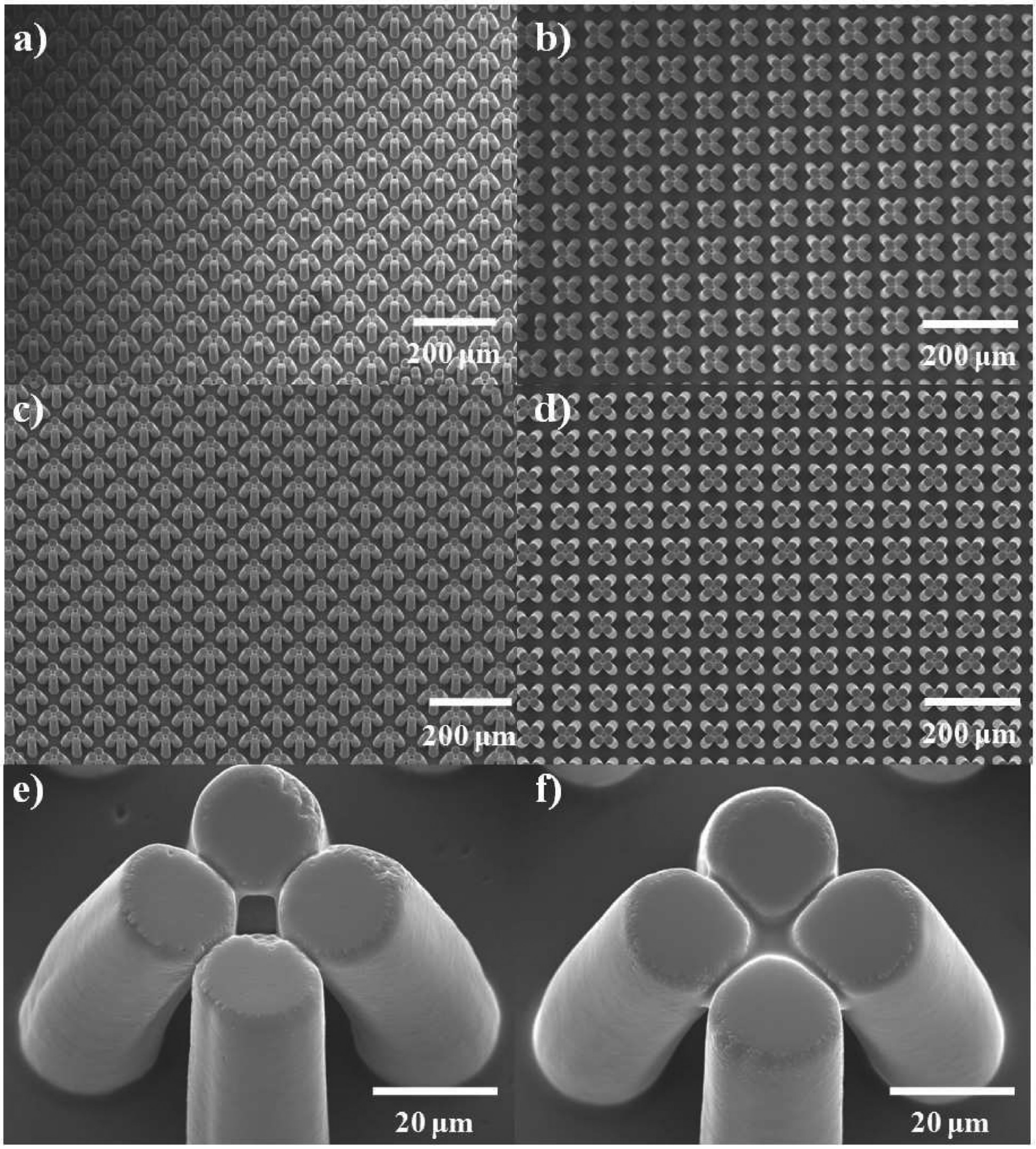

Figure 3. Large arrays of stable microstructures were formed by coating 54 μm tall pillars with (a) 130 nm of PHEMA, (b) 800 nm of PHEMA, (c) 80 nm of PMAA, and (d) 250 nm of PMAA. (e, f) Close-up views of samples c and d showing solvent bonds between the pillars.

Table 1. Opening Time in Blends of Acetonitrile in Methanol (% w/w)

	opening time (s)				
PHEMA coating thickness (nm)	MeOH	25%	50%	75%	acetonitrile
900	1190	1070	920	15	260
1900	4150	2990	2170	170	560

submerging microstructures formed using PHEMA coatings in mixtures of acetonitrile in methanol (MeOH). The fastest rate was achieved using 75% w/w acetonitrile in MeOH. At this composition, the Hansen solubility parameter of the blend is similar to the Hansen solubility parameter of PHEMA (acetonitrile $\delta_d = 15.3$, $\delta_p = 18.0$, $\delta_h = 6.1$ MPa$^{1/2}$; MeOH[27] $\delta_d = 15.1$, $\delta_p = 12.2$, $\delta_h = 22.24$ MPa$^{1/2}$; and PHEMA[28] $\delta_d = 15.14 \pm 0.68$, $\delta_p = 11.87 \pm 0.33$, $\delta_h = 18.84 \pm 0.37$ MPa$^{1/2}$). The amount of time required for the microstructures to open can also be tuned by changing the thickness of the coating. As shown in Table 1, increasing the thickness of the coating lengthens the opening time of the microstructures. Decreasing the thickness of PHEMA to approximately 100 nm allows the microstructures to open almost instantaneously (<2 s) when submerged in MeOH or acetonitrile.

We examined whether we could control the location of self-assembly by patterning a hydrophobic polymer layer onto a hydrophilic layer. Figure 4a shows a schematic of our patterning process. First a layer of PHEMA was deposited onto the PDMS pillars and then a layer of P*o*NBMA was deposited onto the PHEMA layer. The hydrophobic P*o*NBMA layer was then selectively removed by exposure to UV light through a mask. Exposure to UV light cleaves the nitrobenzyl moieties and

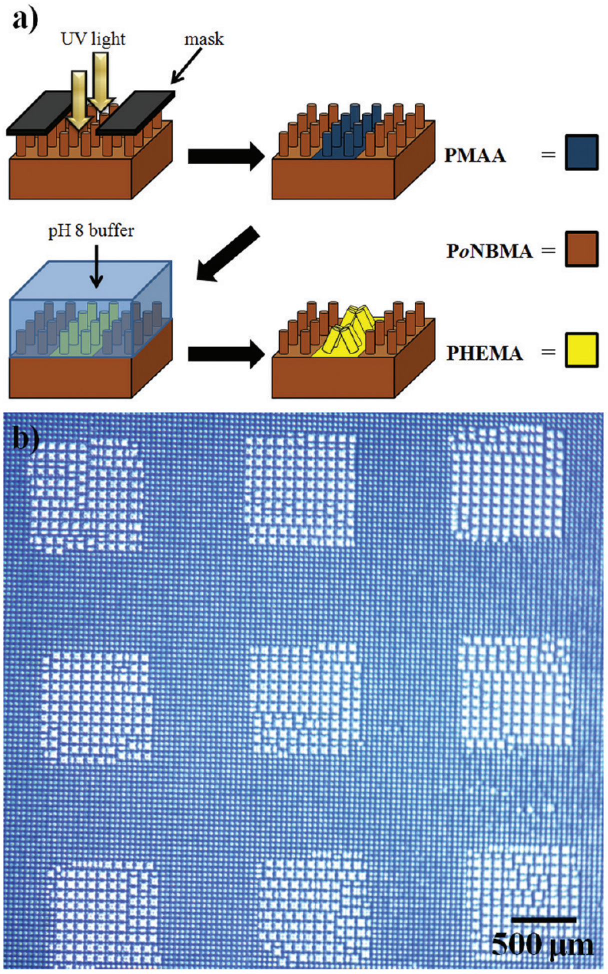

Figure 4. (a) Schematic of the process used to control the location of self-assembly. (b) Stereoscope image showing square regions of collapsed pillars.

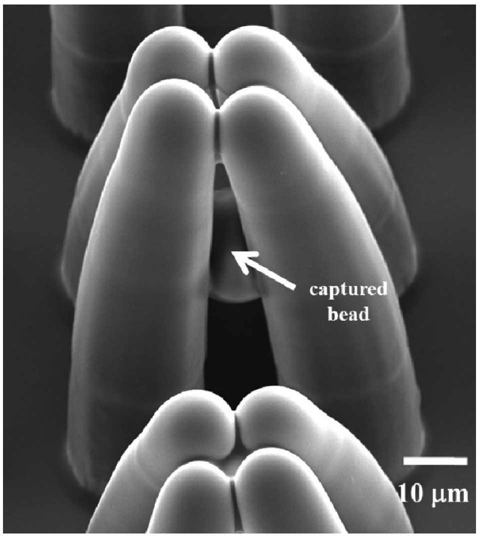

Figure 5. SEM image of a polystyrene bead captured within a microstructure.

converts the exposed P*o*NBMA into PMAA which can be removed in pH 8 buffer solution.[29] The exposed pillars become hydrophilic because of the underlying PHEMA coating, whereas the unexposed pillars remain hydrophobic due to the hydrophobic P*o*NBMA coating. Figure 4b shows that self-assembly occurs only in the hydrophilic regions.

■ CONCLUSION

We demonstrated that iCVD can be used to deposit thin layers of polymer coatings onto pillars and these coatings stabilize self-assembled microstructures by providing an adhesive force through solvent bonding. Furthermore, the location of self-assembly can be controlled through the use of a light-responsive coating. The coating process described in this paper is substrate-independent and therefore can be applied to pillars composed of any material (epoxy, PMMA, carbon nanotubes, etc.). Although micrometer-sized pillars were coated in this paper, the coating process can be extended to nanometer-sized pillars since iCVD has been shown to be effective for coating extremely small dimensions.[30] Future work will determine if temperature-responsive poly(N-isopropylacrylamide) (PNIPAAm) coatings can be used to pattern the location of self-assembly using heat.[31]

The microstructures formed in this study have several potential applications in fields as diverse as microfluidics and drug delivery because the response of the microstructures can be tuned by the thickness of the polymer coating and the solubility parameter of the solvent. Aizenberg and co-workers have suggested that clusters of pillars might be useful for capturing and releasing particles for controlled drug release.[23] Our microstructures are fabricated using biocompatible materials such as PDMS and PHEMA and the tunable time release can be used to control drug doses over a period of time or to sequentially administer multiple drugs.

We are currently investigating whether our microstructures can be used for synthesis within microfluidic devices. For example, catalysts and solid reactants can be entrapped within and released from the microstructures by flowing different solvents through the microchannel. Figure 5 shows our ability to capture beads within our microstructures. Our future work is focused on coating these encapsulated beads within a microchannel and ejecting them using a compatible solvent.

■ EXPERIMENTAL SECTION

Polydimethylsiloxane (PDMS) pillars were made using soft lithography.[32,33] SU-8 2050 photoresist (MicroChem) was patterned onto a silicon wafer using UV light. The pattern consisted of arrays of circular wells. Sylgard 184 (10:1 base to cross-linker ratio) was poured onto the SU-8 mold and cured in an oven at 60 °C overnight. The surface of the SU-8 was treated with trichloro(1H,1H,2H,2H-perfluorooctyl) silane (Sigma Aldrich) to allow the cured PDMS pillars to be easily released.

The PDMS pillars were placed inside a custom designed reaction chamber (GVD Corporation, 250 mm in diameter, 48 mm in height). For poly(2-hydroxyethyl methacrylate) (PHEMA) depositions, 2-hydroxyethylmethacrylate (99%, Sigma Aldrich) was heated to 65 °C and flowed into the reactor at a rate of 0.5 sccm, the reactor pressure was maintained at 0.14 Torr, and the reactor stage was kept at 35 °C. For poly(methacrylic acid) (PMAA) depositions, methacrylic acid (99%, Sigma Aldrich) was heated to 60 °C and flowed into the reactor at a rate of 20 sccm, the reactor pressure was maintained at 0.76 Torr, and the reactor stage was kept at 25 °C. For poly(*o*-nitrobenzyl methacrylate) (P*o*NBMA) depositions, *o*-nitrobenzyl methacrylate (95%, Polysciences) was heated to 110 °C and flowed into the reactor at a rate of 0.1 sccm, the reactor pressure was maintained at 0.12 Torr, and the reactor stage was kept at 20 °C. For all depositions, *tert*-butyl peroxide (TBPO) (Aldrich, 98%) was kept at room temperature and flowed into the reactor at a rate of 0.8 sccm. A nichrome filament array (80% Ni, 20% Cr, Omega Engineering) was resistively heated to 200 °C and the distance between the filament array and the substrate was kept constant at 32 mm. Film thicknesses on reference silicon wafers were determined using interferometry. Contact angle goniometry (ramé-hart model 290-F1) was used to study the wetting properties of the coated pillars.

Pillars coated with PHEMA and PMAA were collapsed into microstructures by dispensing 5 μL of deionized water onto the coated PDMS pillars and allowing the water to evaporate in a covered Petri dish at room temperature. Patterned pillar samples were fabricated by coating PDMS pillars with PHEMA followed by PoNBMA. The pillars were then exposed to 365 nm UV light for 1 h under a transparency mask. After exposure, the samples were developed for 30 s in pH 8 buffer (BDH) and allowed to dry in a covered Petri dish. The tunability of the microstructures was tested using ~0.5 cm^2 microstructure arrays. Residual solvent was removed by placing the samples in a vacuum chamber overnight. The microstructures were then submerged in acetonitrile (Mallinckrodt Chemicals), methanol (Mallinckrodt Chemicals), or a blend of both. Polystyrene beads (20 μm in diameter, 2.5% w/v in water, Polysciences) were mixed at a 1:2 ratio with a 0.25% v/v solution of Triton X-100 (Sigma Aldrich) in methanol. To capture the beads within the microstructures, 5 μL of this solution was dispensed onto a 87 μm tall needle array (0.5 cm^2) coated with 500 nm of PHEMA.

Images were taken using an optical microscope (Meiji ML8000), a stereoscope (National Optical 420 Stereo Zoom), and a low-vacuum scanning electron microscope (JEOL-7001). A thin gold coating was sputtered onto the surface of the samples prior to imaging with the scanning electron microscope.

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