

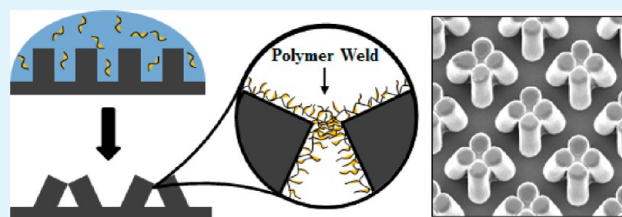
Responsive Polymer Welds via Solution Casting for Stabilized Self-Assembly

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ABSTRACT: We present a simple solution casting technique to apply polymer welds to stabilize capillary-force directed self-assembled systems including arrays of pillars and microbeads. The strength of the polymer welds can be enhanced by increasing either the polymer concentration or molecular weight. The use of responsive polymers to form the welds allow for the fabrication of hierarchical structures that actuate in response to external stimuli. For example, temperature-responsive and pH-responsive microstructures can be formed by solution casting poly(vinyl methyl ether) and poly(methacrylic acid), respectively. We demonstrate that polymer welds formed using biocompatible alginate allows for controllable release of microbeads in microfluidic channels, which has potential applications in drug delivery.

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



INTRODUCTION

The ability to control the formation and stabilization of complex structured arrays is important for device fabrication. For example, capillary forces induced by molten alloys resulted in the self-assembly and bonding of microscale components to form electrical connections.¹ Biomimetic mushroom-shaped adhesive microstructures, inspired by beetles, have been fabricated by molding polymer within a template.² Photonic crystals have been fabricated from ordered arrays of spherical metal nanoparticles.³ Other interesting applications can be realized if the structures are not restricted to a single configuration. For example, ultrathin optical devices can be created by transitioning between a periodic array of pillars exhibiting Bragg diffraction and self-assembled clusters of pillars that scatter light randomly to create a whitening effect,⁴ similar to that of the white beetle.⁵ Additionally, the reversible adhesion of gecko feet has been replicated in biomimetic studies.^{6,7}

Matsunaga et al. has developed actuable microstructures using self-assembled monolayers (SAMs) as a reversible adhesive layer,⁸ and we have recently demonstrated that polymer coatings deposited via vapor phase polymerization (VPP) can be combined with appropriate solvents to control the assembly and disassembly of microstructures.⁹ The formation of SAMs requires the use of specific chemistries between the substrate and corresponding head groups, while VPP requires specialized and expensive equipment (mass flow controllers, pumps, and heat exchangers), limiting these techniques to a few laboratories. In this paper, we demonstrate for the first time a cheaper and simpler solution casting method to form polymer welds that stabilize self-assembled features. A polymer solution is applied to a system of discrete objects and

then allowed to evaporate. During evaporation, capillary forces pull the objects together and induce self-assembly. As the polymer solution becomes increasingly concentrated, the polymer chains interdiffuse and solidify to form a polymer weld that stabilizes the self-assembled structures. An added benefit of our method compared to the VPP technique is that virtually any polymer can be used as long as a suitable solvent is utilized. Responsive systems can be formed using polymers that are known to experience drastic property changes due to environmental stimuli such as temperature,¹⁰ pH,¹¹ light,¹² and electrical signal.¹³ We demonstrate the versatility of our technique by forming pH-responsive and temperature-responsive microstructures from arrays of poly(dimethylsiloxane) (PDMS) pillars and by adhering and selectively releasing poly(styrene) microbeads within a microfluidic channel. A diverse set of polymers can be solution casted including biocompatible materials such as alginate and poly(2-hydroxyethyl methacrylate), which allows our technique to be extended to biomedical applications such as tissue engineering and drug delivery. Furthermore, the simplicity of our experimental procedure allows it to be used universally in every laboratory.

RESULTS

A simple polymer solution casting technique was used to self-assemble pillars into microstructures stabilized by polymer welds. The welds are formed by taking advantage of capillary forces combined with interdiffusion and solidification of the

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polymer during solvent evaporation. The general process is outlined in Figure 1. As the solvent evaporates, the liquid level

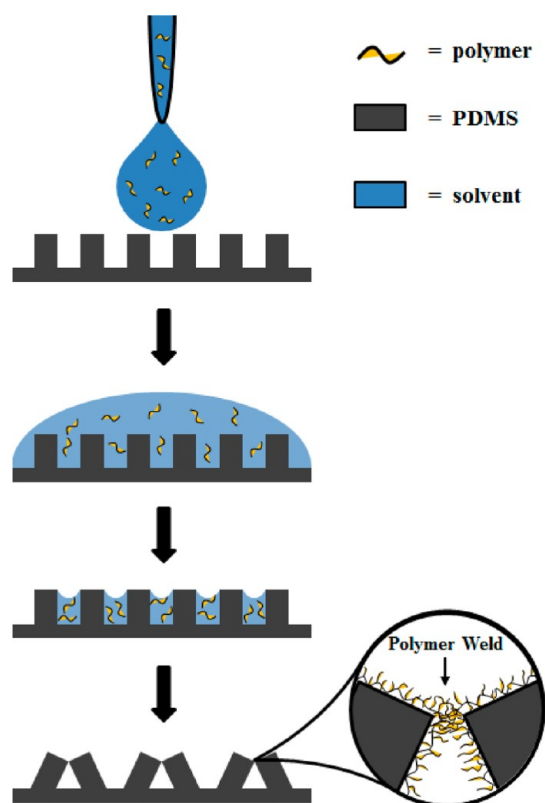


Figure 1. Schematic showing the self-assembly of pillars and the formation of polymer welds by solution casting.

falls below the height of the pillars, resulting in capillary forces that pull the pillars into contact. The formation of microstructures requires that the capillary forces be strong enough to cause the pillars to make contact. The capillary force on an individual pillar in a system of four pillars is given by¹⁴

$$F_{\text{cap}} = \frac{\pi\gamma d^2 \cos^2 \theta}{2} \left(\sqrt{\frac{2}{(p - 2\delta)^2 - d^2}} + \sqrt{\frac{1}{2(p - 2\delta)^2 - d^2}} \right)$$

where γ is the liquid-vapor surface tension, d is the diameter of the pillars, θ is the contact angle of the solution on the pillar material, p is the distance between the centers of adjacent nondiagonal pillars, and δ is the deflection distance of the pillar. As the pillars deflect, the capillary forces are resisted by the net elastic restoring force of the pillars. The elastic restoring force of a single pillar is given by¹⁵

$$F_{\text{elastic}} = \frac{3\sqrt{2}\pi E d^4 \delta}{64h^3}$$

where E is the elastic modulus of the pillar material and h is the height of the pillar. If the capillary force is large enough to overcome the elastic restoring force, adjacent pillars will be brought into contact with one another. Once the solvent completely evaporates, capillary forces are no longer present to overcome the elastic restoring force; therefore, an adhesive force must be introduced to stabilize the microstructures. In

our system, the adhesive force is provided by a polymer weld that forms at the interface between the pillars while they are in contact. Figure 2 shows our ability to form stable microstructures by solution casting nonpolar, polar, and charged polymers of various molecular weights (MW) onto an array of PDMS pillars. A volume of 10 μL of 0.5% w/w poly(styrene) (4 000 MW) in acetone, poly(methyl methacrylate) (50 000 MW) in acetone, poly(2-hydroxyethyl methacrylate) (20 000 MW) in methanol, and alginate in water were solution casted onto 0.7 cm \times 0.7 cm arrays of PDMS pillars. The PDMS pillars were 60 μm in height and 22 μm in diameter with a spacing of 18 μm between the edges of the pillars as measured from scanning electron microscopy (SEM) images. Depending on the substrate and solvent combination used during solution casting, wettability may be an issue. In order to overcome surface tension effects, we irradiated our PDMS pillars with air plasma using a hand-held corona generator to increase hydrophilicity prior to wetting the pillars with aqueous solutions.

We can control the quality of adhesion via the solution casting method. The polymer weld must resist the total elastic restoring force of all the pillars forming the microstructure. Therefore, higher-ordered microstructures require a stronger polymer weld to counteract the increased elastic restoring force due to additional contributing pillars and longer deflection distances. For example, we have observed that during self-assembly, a microstructure formed by a cluster of four pillars will detach into two clusters of two pillars when a polymer weld is too weak. The sizes of microstructures formed are indicative of the relative strength of the polymer welds. We tested the sensitivity of the polymer welds to changes in concentration and molecular weight as shown in Figure 3. Starting near solution saturation, 10 μL quantities of 500 000 MW poly(methyl methacrylate) in acetone at weight percentages of 5×10^{-1} down to 5×10^{-5} were applied onto the arrays of PDMS pillars. Solutions with weight percentages of 5×10^{-1} and 5×10^{-2} consistently produced arrays of microstructures predominantly consisting of clusters of four pillars. At 5×10^{-3} w/w, the adhesion weakened and we observed several detached clusters of four pillars yielding clusters of two pillars while some pillars remained singular, failing to form microstructures of any order. At lower dilutions, the adhesion was too weak to stabilize clusters of any size. The increased adhesion at greater polymer concentrations is likely due to the formation of thicker welds, which has been confirmed by SEM. These experiments were repeated using lower molecular weights (50 000 MW and 5 000 MW) at the same dilutions. As shown in Figure 3, at 5×10^{-2} w/w the 50 000 MW solution continued to produce clusters of four pillars; whereas, the 5 000 MW solution produced clusters of two and four pillars. Diluting the poly(methyl methacrylate) concentration below 5×10^{-3} w/w yielded less clusters for both 5 000 MW and 50 000 MW compared to 500 000 MW. Further dilution failed to produce any significant number of structures. These results indicate that solutions with lower molecular weight polymers produce less microstructures compared to solutions with higher molecular weight polymers at similar weight percentages. SEM images of these structures revealed that thicker welds are formed when larger molecular weights are used. The formation of thicker welds is likely due to increased viscosities at higher molecular weights¹⁶ resulting in greater polymer accumulation at the pillar interface upon evaporation,

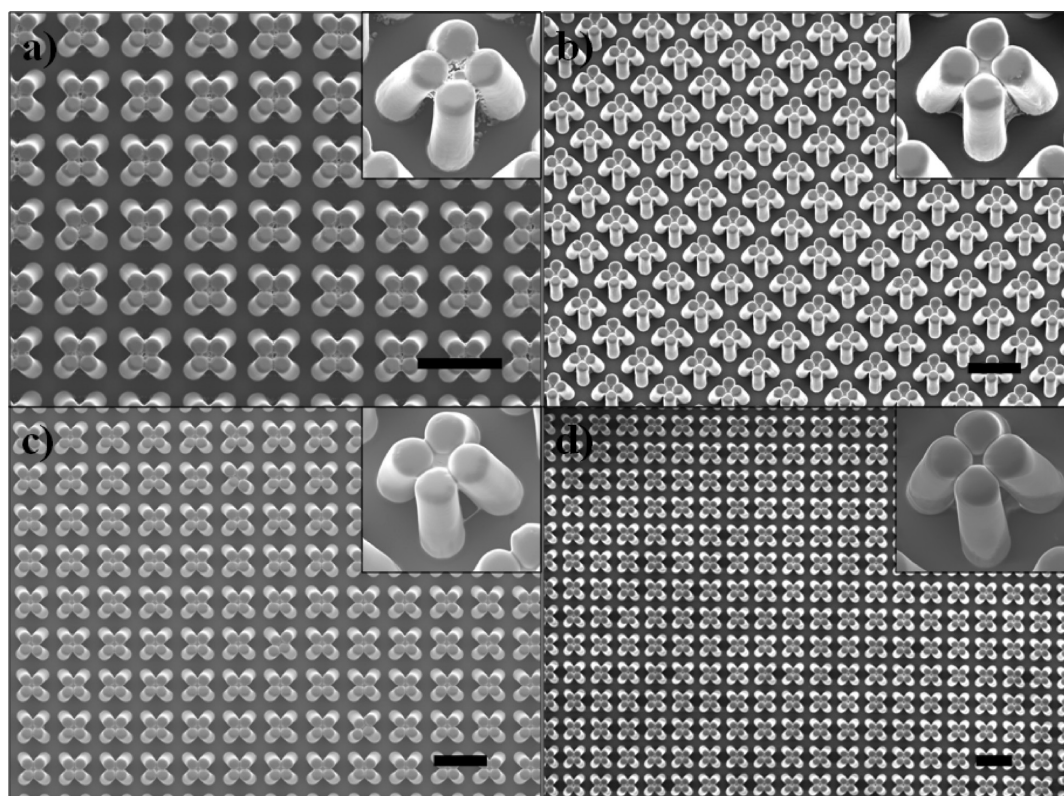


Figure 2. SEM images of PDMS microstructures stabilized by polymer welds formed from (a) poly(styrene), (b) poly(methyl methacrylate), (c) poly(2-hydroxyethyl methacrylate), and (d) alginate. All scale bars represent 100 μm in length.

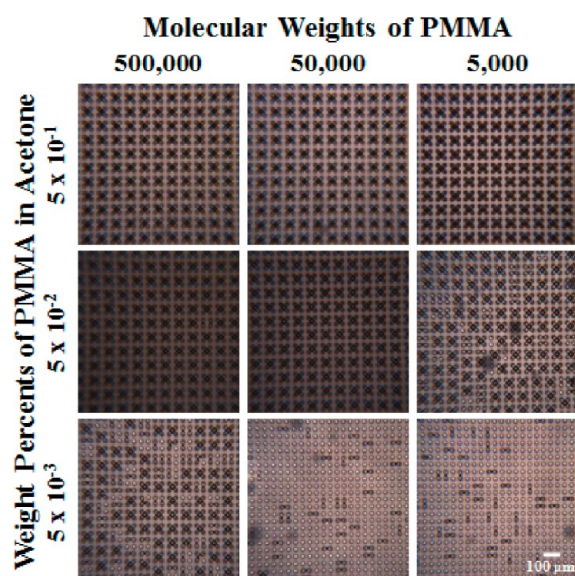


Figure 3. Microscope images of PDMS microstructures showing increasing cluster formation with greater molecular weight and concentration.

similar to dip coating processes where greater viscous forces lead to thicker films.¹⁷

Generally, polymer welds are formed by placing a solvent between two surfaces of the same material and applying pressure to form a weld composed of the same material as the surface. For example, poly(methyl methacrylate) microfluidic channels can be bonded by placing acetone¹⁸ or a mixture of dichloroethane and ethanol¹⁹ between the surfaces. In our

system, two similar surfaces are adhered together by a dissimilar polymer. The polymer must be compatible with the substrate in order to form a strong polymer weld. To examine this, we attempted to use our solution casting technique on PDMS pillars coated with a low surface energy fluoropolymer, poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate-*co*-ethylene glycol diacrylate) (P(PFDA-*co*-EGDA)). These coated pillars resisted the formation of polymer welds in all tested polymer-solvent systems which included 0.5% w/w solutions of poly(styrene) in acetone, poly(methyl methacrylate) in acetone, poly(2-hydroxyethyl methacrylate) in methanol, and alginate in water. A possible concern is that the fluorinated coating may change the capillary forces and thereby prevent the pillars from making contact. However, we used optical microscopy to confirm that the pillars made contact and then separated as capillary forces diminished in each case. The fluoropolymer coating prevents the diffusion of the solvent into the PDMS;²⁰ therefore, the PDMS remains immobilized during the welding process. C. Y. Yue has shown that the adhesion of dissimilar polymer welds such as poly(vinyl chloride)-poly(methyl methacrylate) and poly(vinyl chloride)-poly(carbonate) are significantly enhanced when both interfaces are mobilized during the solvent welding process.²¹ By preventing polymer interdiffusion with the PDMS substrate, adhesion depends only on the interaction between the P(PFDA-*co*-EGDA) surface and the solution casted polymer, which is weak due to the fluorinated pendant groups in the coating.

A major advantage of polymer welded microstructures is the ability to use specific external stimuli to reverse the self-assembly. The microstructures remain intact when washed with an incompatible solvent and disassemble when the polymer weld is dissolved by a compatible solvent. For example,

microstructures formed using poly(styrene) remained stable when washed with methanol but disassembled when washed with acetone. However, polymer weld dissolution is not restricted to weak intermolecular interactions. For example, electrostatic interactions can be used to control the dissolution of a weld with pH-sensitive moieties. This concept is demonstrated in Figure 4 where reversible pH-responsive

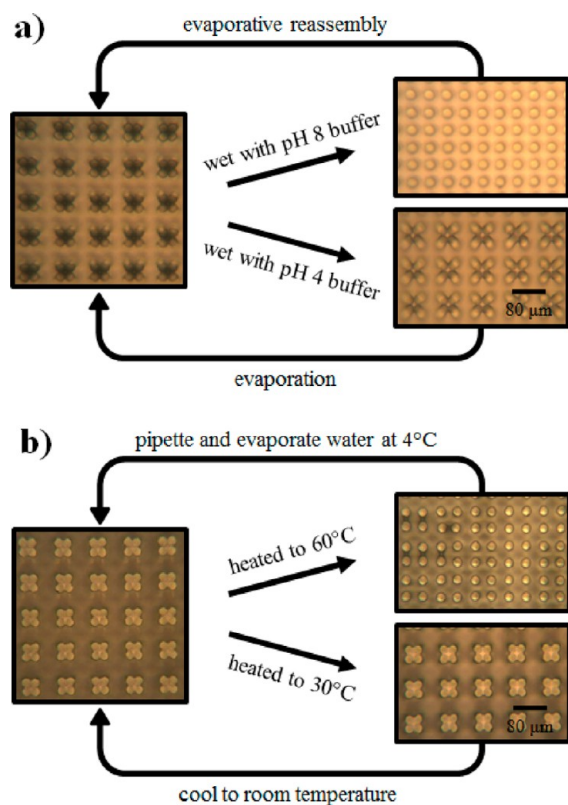


Figure 4. Schematics showing microstructures that respond to variations in (a) pH value and (b) temperature.

microstructures were created by solution casting poly(methacrylic acid) (100 000 MW) in methanol onto shorter 54 μm tall PDMS pillars. Shorter pillar heights were used in order to increase the elastic restoring force which resulted in faster disassembly rates. To test the dissolution of our polymer welds at low pH, we submerged the stabilized microstructures in pH 4 buffer for 3 h, after which the polymer welds remained intact, allowing the microstructures to remain assembled. When these microstructures were submerged in neutral water, the poly(methacrylic acid) dissociated causing the welds to dissolve and the microstructures to revert back to an upright position. The disassembly process using neutral water occurred within 30 minutes but could be expedited to approximately 1 minute by submerging the structures in pH 8. After disassembly, the pillars reassembled back into microstructures during evaporation of the buffer. Prevention of reassembly can be achieved by washing the samples with copious amounts of pH 8 buffer to remove the polymer.

Certain devices, such as microelectronics,^{22,23} are sensitive to the presence of solvents, and therefore, a solventless method for actuation may be desired. When a linear polymer is heated far beyond its glass transition temperature, the chains become mobilized and the modulus of the polymer decreases rapidly.²⁴ We used this concept to create temperature-responsive

microstructures that do not require solvents for actuation. These microstructures were fabricated by solution casting poly(vinyl methyl ether) in water onto the shorter 54 μm PDMS pillars in a refrigerator set to 4°C (Figure 4). Since poly(vinyl methyl ether) has a low glass transition temperature (~ -31 °C),²⁵ the formation of stable microstructures is difficult at room temperature due to residual solvent weakening the weld. Conducting the self-assembly process at lower temperatures increases the modulus of the polymer so that the newly formed welds can stabilize the microstructures while residual solvent evaporates. After the residual solvent is removed, the polymer weld is strong enough so that the microstructures remain stable when brought to room temperature. When the microstructures were heated to 30 °C, they remained stable; whereas, far beyond the glass transition temperature at 60 °C, they disassembled within 20 minutes. A much faster disassembly time of 5 minutes was achieved at 90 °C. After disassembly, the microstructures could be reformed via the addition of 10 μL of water in a refrigerator (4°C) to recreate the solution casting process.

The formation of a polymer weld by evaporating a polymer solution at an interface is not restricted to pillars. Theoretically, any combination of compatible interfaces that can be brought into contact by capillary forces can be stabilized by our welding process. For example, we used the solution casting process to self-assemble microbeads within an array of microstructures by simultaneously collapsing pillars and capturing beads (Figure 5a). This assembly was performed by applying a suspension of

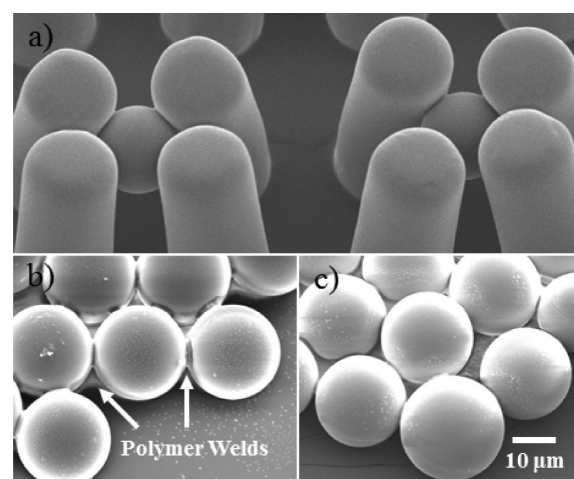


Figure 5. SEM images showing variations of alginate weld formation around poly(styrene) microbeads. (a) Microbeads were captured and welded within microstructures. On flat PDMS, welds were formed (b) underneath the beads and between adjacent beads at 0.3% w/w, (c) whereas welds were formed only between adjacent beads at 0.03% w/w.

polystyrene microbeads in an alginate–water solution onto an array of pillars, forming welds between the bead and pillar interfaces upon evaporation. Additionally we used polymer welds to create responsive microbead release systems. Poly(styrene) microbeads were self-assembled and welded onto flat PDMS and within microfluidic channels by evaporating aqueous solutions of alginate containing a suspension of the microbeads. The formation of polymer welds between beads and various substrates is similar to the formation of welds between pillars, where capillary forces draw the evaporating

polymer solution towards the interfaces of adjacent beads where the polymer interdiffuses, solidifies, and forms a weld. Prior to solution casting, the PDMS surface was treated with air plasma to enhance wetting of the solution on the substrate. Depending on the concentration of the polymer solution, the polymer welds can form at different locations around the beads as shown in Figure 5b,c. Adjacent beads were welded to each other and to the underlying PDMS substrate by pipetting 15 μL of an aqueous mixture containing 0.3% w/w alginate and 1.7% w/w 20 μm poly(styrene) beads. However, when the alginate concentration was diluted to 0.03% w/w, the microbeads were welded to adjacent beads but not to the PDMS substrate. In order to ensure the release of microbeads in our system, a weld separating the bead from the substrate is necessary. If microbeads make contact with the substrate, they could become adhered to it through adhesive forces such as van der Waals attraction. For example, our poly(styrene) microbeads that were directly in contact with the PDMS could not be released by dissolving the alginate with water due to the attraction of the beads to the surface. However, microbeads that were separated from the PDMS surface by alginate were easily removed from the surface by the addition of water.

A demonstration of the use of solution casting to adhere and selectively release beads within microfluidic channels is shown in Figure 6. Microbeads were self-assembled by injecting and

swell causing greater separation between the beads until finally the alginate welds dissolved, releasing the beads.

CONCLUSION

We have demonstrated a simple, robust solution casting technique to stabilize capillary-force directed self-assembled systems using polymer welds. A wide variety of polymer solutions were used to stabilize arrays of PDMS microstructures and to control the adhesion of microbeads within microfluidic channels. The strength of the polymer welds was systematically tuned by either increasing the molecular weight of the polymer or by increasing the solution concentration. Utilizing different polymers created reversible, environmentally-responsive systems. Temperature, pH, and solubility were used to control the assembly, disassembly, and reassembly of the microstructures. The simplicity of our experimental procedure allows it to be used universally and tailored for specific applications due to the vast number of commercially available polymers. For example, the use of aqueous solutions of biocompatible polymers such as alginate and poly(2-hydroxyethyl methacrylate) allows our technique to be used in biomedical applications such as drug delivery and tissue engineering.

EXPERIMENTAL SECTION

PDMS pillars and microchannels were fabricated using standard photolithography and soft lithography techniques. A master mold was fabricated by spin coating SU-8 2050 photoresist (MicroChem) for the pillar arrays and SU-8 50 photoresist (MicroChem) for the microchannels onto a silicon wafer and exposing it to UV-light through an emulsion transparency mask (CAD/Art Services, Inc.). Afterwards, trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane (Sigma Aldrich) was deposited onto the mold using a desiccator to ensure the easy release of cured PDMS. Sylgard 184 was mixed at a 10:1 base to cross-linker ratio, poured onto the mold, and thermally cured at 60 $^{\circ}\text{C}$ for 4 h. The microchannels were assembled by oxidizing the channel piece and a flat slab of PDMS with a corona generator (BD20-AC, Electro-Technic Products, Inc.), bringing both layers together in intimate contact, and curing the device in an oven at 65 $^{\circ}\text{C}$ for 4 h.

The PDMS pillars were self-assembled by pipetting 10 μL of polymer solution onto a 0.7 cm \times 0.7 cm array. The pillars were 60 μm in height and 22 μm in diameter with a spacing of 18 μm between the edges of the pillars. The polymer solutions were composed of 0.5% w/w polymer solutions of alginic acid sodium salts (Sigma Aldrich) in deionized water, poly(methyl methacrylate) (Varian GPC standards 5 000, 50 000, and 500 000 MW) in acetone, poly(styrene) (Fluka GPC standard 4 000 MW) in acetone, and poly(2-hydroxyethyl methacrylate) (Sigma Aldrich 20 000 MW) in methanol. Optical microscopy images were taken using a Meiji ML8000 microscope, and SEM images were taken using a JEOL 7001 scanning electron microscope. Prior to SEM imaging, all samples were coated with a thin layer of gold via sputtering.

In order to test different degrees of compatibility between the polymer weld and the substrate, arrays of PDMS pillars were coated with a thin layer of poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate-co-ethylene glycol diacrylate) in a custom designed initiated chemical vapor deposition (iCVD) chamber (GVD Corp, 250 mm diameter, 48 mm height) as described previously.²⁰ While maintaining the pressure at 65 mTorr, 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate (SynQuest, 97%), ethylene glycol diacrylate (Monomer-Polymer, 90%), and di-*tert*-butyl peroxide (Sigma-Aldrich, 98%) were flowed into the chamber at 0.3, 0.8, and 1.2 sccm, respectively. The di-*tert*-butyl peroxide initiator was thermally decomposed into free radicals by a heated wire array (220 $^{\circ}\text{C}$), and the monomer and initiator radicals were adsorbed to the cooled substrate (30 $^{\circ}\text{C}$) and polymerized via a free radical chain mechanism.

pH-responsive microstructures were formed using a 0.35% w/w aqueous solution of poly(methacrylic acid) (Polysciences 100 000

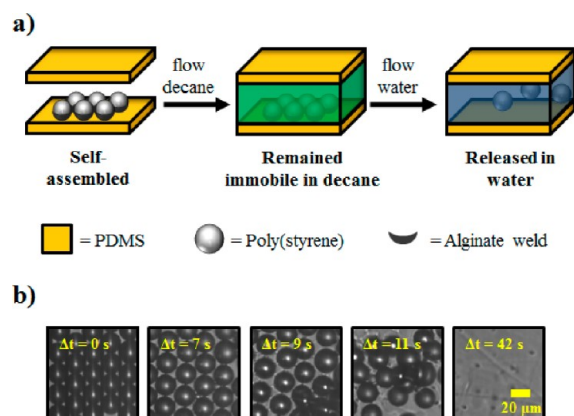


Figure 6. (a) Schematic showing controlled release of self-assembled microbeads within a microfluidic channel using different solvents. (b) Time series of microscope images showing the release of poly(styrene) microbeads welded with alginate by flowing water within a microfluidic channel.

then evaporating an aqueous solution of 0.6% w/w alginate containing a 6% w/w suspension of 20 μm poly(styrene) beads into a microfluidic channel with a cross sectional area of 300 μm \times 1000 μm . A polymer concentration of 0.6% w/w was used to ensure that the beads were welded to the underlying PDMS. When an incompatible solvent such as decane or hexane was flowed through the channel, the particles remained adhered to the PDMS due to the inability of the solvents to dissolve the polymer welds. However, when a compatible solvent such as water was flowed through the channel, the polymer welds dissolved and the beads travelled freely down the channel. Images showing the details of the release process are shown in Figure 6. When water was flowed into the channel, the polymer welds were clearly visible at the interfaces of the hexagonally packed poly(styrene) beads. As the water incorporated itself into the polymer welds, the welds began to

MW). Prior to forming the solution, 500 mg of poly(methacrylic acid) was soaked in 10 mL of deionized water for 2 minutes and filtered using grade 413 filter paper (VWR). The resultant solution was then dried and redissolved in deionized water to form 0.35% w/w solution. The pH-responsive microstructures were self-assembled by pipetting 10 μL of the solution onto PDMS pillars that were 54 μm tall, 22 μm in diameter, and separated by 18 μm of spacing between the edges of the pillars. In order to test the responses of the microstructures at different pH values, the structures were treated with a corona generator and then wet with 20 μL of either deionized water, pH 8 buffer (BDH) or pH 4 buffer (BDH). Temperature-responsive microstructures were formed by pipetting 20 μL of a 1% w/w solution diluted from a 50% w/w stock aqueous solution of poly(vinyl methyl ether) (Sigma Aldrich) onto pillars treated with a corona generator. Fast and slow disassembly of the poly(vinyl methyl ether) stabilized microstructures was performed by placing them into a preheated oven set to 90 $^{\circ}\text{C}$ for 5 minutes and 60 $^{\circ}\text{C}$ for 20 minutes, respectively. Stability at lower temperatures was tested in an oven set at 30 $^{\circ}\text{C}$ for 20 minutes.

The capture of microbeads within microstructures was performed by pipetting 15 μL of an aqueous mixture containing 0.03% w/w alginate and 1.7% w/w 20 μm polystyrene microbeads onto a 0.7 cm \times 0.7 cm array of pillars with a height of 60 μm . Microbeads were adhered onto flat PDMS by pipetting 15 μL of an aqueous mixture containing 0.3% w/w or 0.03% w/w alginate and 1.7% w/w 20 μm polystyrene microbeads onto a 0.7 cm \times 0.7 cm flat PDMS substrate. The adhesion of the microbeads was tested under an optical microscope while pipetting 50 μL of water onto the surface of the sample. SEM images were taken after sputtering a thin layer of gold onto the samples. The self-assembly of microbeads within a microfluidic channel was performed by slowly injecting an aqueous mixture containing 0.6% w/w alginate and 6% w/w poly(styrene) microbeads into the channel by hand. The solvent was allowed to evaporate at ambient conditions. The controlled release of the microbeads was performed by injecting the desired solvents at 2 mL h^{-1} ($U = 6.67 \text{ mm s}^{-1}$) into the channel using syringe pumps. Images were collected at 10.26 frames per second on a Nikon (Tokyo, Japan) TI-E inverted microscope.

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Notes

The authors declare no competing financial interest.

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