

Robust polymer microfluidic device fabrication *via* contact liquid photolithographic polymerization (CLiPP)[†]

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Microfluidic devices are commonly fabricated in silicon or glass using micromachining technology or elastomers using soft lithography methods; however, invariable bulk material properties, limited surface modification methods and difficulty in fabricating high aspect ratio devices prevent these materials from being utilized in numerous applications and/or lead to high fabrication costs. Contact Liquid Photolithographic Polymerization (CLiPP) was developed as an alternative microfabrication approach that uniquely exploits living radical photopolymerization chemistry to facilitate surface modification of device components, fabrication of high aspect ratio structures from many different materials with numerous covalently-adhered layers and facile construction of three-dimensional devices. This contribution describes CLiPP and demonstrates unique advantages of this new technology for microfabrication of polymeric microdevices. Specifically, the procedure for fabricating devices with CLiPP is presented, the living radical photopolymerization chemistry which enables this technology is described, and examples of devices made using CLiPP are shown.

Introduction

Fabrication strategies for microdevices, particularly microfluidic devices, that perform tasks including separation, analysis and detection of biological and chemical compounds (e.g. "labs-on-a-chip"), have drawn considerable research interest and investment in the past decade.^{1–6} Although many microfluidic devices are fabricated in silicon or glass, polymers provide a wider range of chemical and physical properties and surface modification options than inorganic materials.^{7–9} However, because they are constructed from one layer of a single polymer selected from a relatively small set of processable precursors, microdevices made *via* common polymer fabrication techniques^{7,8} (including soft lithography,^{10–15} injection molding,^{16,17} hot embossing¹⁸ and thick photoresist patterning^{19,20}) often fail to exploit the full spectrum of material properties and tailorable functionality. To date, the drawbacks of devices made from traditional inorganic microfabrication technologies and emerging polymer fabrication methods have limited commercialization and broad application of microfluidics-based solutions.

Direct photolithographic patterning of photocurable materials through a combination of photopolymerization technology and highly controlled light exposure (e.g. rastering a focused source or flood exposure through a mask, among others) is a promising and straightforward method for fabrication of polymeric microdevices. Implementation of

photopolymers directly for microdevice fabrication is an avenue that has been explored but not widely implemented as a microfabrication technology. Beebe and coworkers^{21,22} fabricated channels, valves and pumps for microfluidic systems using photopolymerization of multifunctional monomers to form hydrogel networks (*i.e.* loosely crosslinked hydrophilic polymers that swell in the presence of water) into hydrophobic polymer channels. Furthermore, Beebe and others have used photopolymerizations of liquid monomer formulations contained within prefabricated cartridges to form microchannels in highly crosslinked polymers.^{23,24} Researchers have used direct photopolymerization of monoliths within channels to form microfluidic valves²⁵ and separations or combinatorial chemistry platforms.^{26–28} Finally, other groups have used direct photopolymerization of ceramic precursor monomers to create devices for high temperature applications.^{29,30} Each of these examples is well suited for the parallel fabrication of many single layer devices or components, but none enable facile construction of many multilayer devices with *in situ* formed vias and well-adhered layers. Conversely, serial production methods such as microstereolithography,^{7,31,32} two photon polymerization^{33–35} and direct write assembly³⁶ facilitate construction of geometrically complex *individual* structures, but are not feasible for efficient fabrication of more than a small number of microdevices.

Living radical photopolymerization (LRPP) is one underlying technology that will enable facile, parallel fabrication of geometrically-complex multilayer devices. LRPP, which exploits specific initiator chemistries that continuously reactivate during exposure to UV light, has been implemented for synthesizing linear polymers with well-defined molecular weight and/or polymer chain architecture.³⁷ Ideally, growing polymer chain ends are never permanently terminated or

[†] Electronic supplementary information (ESI) available: tables displaying details of typical monomer formulation and materials for CLiPP fabrication and a figure displaying a cogwheel mask set. See <http://www.rsc.org/suppdata/loc/b4/b405985a/>

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deactivated. In conjunction with crosslinking monomers, LRPP enables initiation and covalent adhesion of new polymer chains or films to the surfaces of previously photopolymerized films.^{38–40}

This contribution introduces a direct photolithographic patterning technology, Contact Liquid Photolithographic Polymerization (CLiPP), which uniquely incorporates LRPP for polymer microfabrication. CLiPP combines fundamental principles of silicon micromachining (*e.g.* photolithography and sacrificial layers) with polymeric materials and unique initiation chemistry to create microdevices with highly complex three-dimensional architectures and extremely versatile surface and bulk physical and chemical properties. The unique advantages of this novel technology are demonstrated and include facile parallel fabrication of multilayer microfluidic devices that are particularly suitable for many chemical and biological separations, analyses and detection schemes. Specifically, different preformed materials (*e.g.* filters) or photopolymerizable monomer formulations can be incorporated within individual layers and/or devices; adjacent layers are covalently adhered, connections between layers are formed *in situ*, and surface chemical properties can be spatially modified *via* tethered polymer chains. Finally, CLiPP is an enabling technology for constructing microscale polymeric platforms and components that is well suited for rapid prototyping and large scale fabrication.

Materials and methods

The supplementary information available from the publisher website includes tables containing a typical monomer formulation for fabricating base structures and a partial list of monomers available for integration within microdevices fabricated with CLiPP to impart various physical, chemical and mechanical properties.† Monomer formulations were cured with a 5 cm collimated flood exposure source, which was coupled to an optical mask alignment system (Optical Associates, Inc., San Jose, CA), which generated 50–70 mW cm⁻² of 365 nm radiation. An adjustable reaction chamber facilitated well-defined control of individual layer thickness. Specifically, the spacing between the photomask and chamber bottom was controlled by micromanipulators coupled to a height sensor and the entire reaction chamber was integrated with the theta and lateral controls of the mask aligner.⁴¹ Masks were made using emulsion films (Polychrome V; Kodak, Rochester, NY) exposed with a high-resolution helium–neon red laser diode commercial plotter.

Typically, layers of monomer formulations containing a photoiniferter precursor, tetraethylthiuram disulfide (TED), reached maximum conversion in one to five minutes of flood exposure. Unexposed regions were readily cleaned with methanol and if necessary, refilled with molten wax (*e.g.* Paramat Extra; Electron Microscopy Sciences, Fort Washington, PA) to planarize the surface for introduction of monomer and flood exposure to construct a subsequent layer. Upon completion, the wax was removed by heating the device to *ca.* 70 °C, applying positive or negative pressure, and rinsing with solvent (*e.g.* CitriSolv; Fisher Scientific, Fairlawn, NJ). Devices requiring wax for undercut geometries were designed with continuous channels and/or ports to allow removal of the molten wax upon completion.

Description of CLiPP technology

Fig. 1 depicts the four general steps that are necessary to fabricate three-dimensional polymeric devices. Firstly, intralayer-specific material properties are chosen by altering the composition of the monomer formulation. Secondly, a photomask is contacted with the liquid monomer solution. The

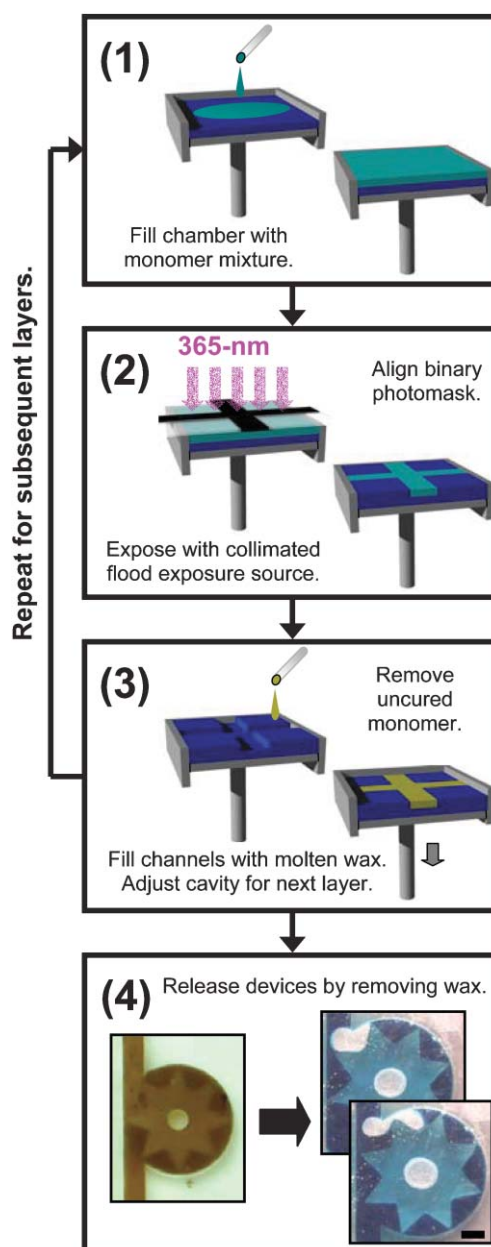


Fig. 1 Schematic of the CLiPP process. Step 1: a monomer mixture completely fills a chamber formed from a stainless steel box, an adjustable-height base plate, and a binary photomask. Step 2: the monomer mixture is exposed to 365 nm UV radiation through an aligned, contacted photomask. Step 3: uncured monomer is removed from the layer and molten wax fills voids to prepare a level surface for subsequent layers. The height of the chamber base is adjusted and steps 1 to 3 are repeated for each subsequent layer. Step 4: upon completion, the device is released from the polymerization chamber and the wax is removed. The picture shows a cogwheel that was fabricated from five layers. Wax (brown) was used to planarize each layer prior to depositing additional monomer. After removal of the wax, the wheel spins around a fixed axle when a fluid (blue) is pumped through the channel on the left side. Scale bar, 1 mm.

thickness is adjusted prior to flood exposure, leading to three dimensions of spatially controlled polymerization. Thirdly, unreacted monomer is removed from the cured film, and if necessary, trenches are filled with molten wax to prepare a level surface. The first three steps are repeated for each subsequent layer. Finally, devices are released from the substrate, and void regions are cleared by removal of the sacrificial material.

Step 1 illustrates the selection of a monomer formulation and filling the reaction chamber. This process enables control of the chemical and mechanical properties of each individual subunit

within the device (*e.g.* channels, valves, separation media *etc.*) via the rich chemistry of vinyl-containing monomers available for creating structures within each layer. Multi- and monovinyl compounds that have been successfully photopolymerized in this fashion include styrene-polyesters, (meth)acrylates, vinyl ether-maleates, maleimides, and thiol-enes.^{42–45} Additionally, a number of formulations containing inorganic components can also be photopolymerized to impart specific functionality.^{29,30} Furthermore, monomers are not limited by incompatibility with adjacent surface layers or high viscosity because they are physically contained within an enclosed, variable-depth well during the curing step. Layer and subunit chemical and mechanical properties are readily tailored to impart unique characteristics by rational selection of monomers with specific spacers between functional groups and desirable side chain chemistry. Monomer selection impacts polymer properties such as optical clarity, modulus, toughness, degradation kinetics, barrier and swelling properties, and specific reactions with analytes or reagents.

Living radical photopolymerization

The CLiPP process depends on unique photoinitiator chemistry, *i.e.*, photoiniferter moieties, available at the surfaces of cured layers for two distinct properties. Firstly, adhesion between adjacent layers is critical for device performance. However, physical bonding between layers is not sufficient for complex devices fabricated from multiple monomers; frequently, covalent bonding between layers is necessary. Secondly, many functions performed in microfluidic devices rely upon interactions between fluids and transported chemical or biological compounds with the inner surfaces of the device. Often, spatially controlled surface properties that differ from the bulk material properties are desirable. Incorporation of a living radical initiator (*i.e.* iniferter) in the monomer formulations used for various layers and subunits within a device enables spatially resolved grafting or modification *via* photolithographic methods and surface-mediated LRPP.

Fig. 2 shows the two primary functions of the iniferter-containing layers: surface-mediated grafting (top route), or covalent adhesion of an adjacent layer (bottom route). Specifically, layers formed from monomer formulations containing iniferter precursors have photocleavable groups (*i.e.* dithiocarbamate moieties, DTC) at their surfaces that initiate polymerization of other monomers upon illumination.^{37–40,46,47} A variety of monomers has been incorporated in this manner, yielding hydrophilic or hydrophobic surfaces, as well as surfaces with a high ionic content suitable for driving electro-osmotic flow. In the case of initiating monovinyl monomers from a DTC-containing surface, the radiation dose controls the concentration of the surface grafted polymer.^{38,39} In fact, strict control of the grafted polymer architecture is not facilitated by the photoiniferter method.^{38,39} Nonetheless, controlled polymerization is less important than the ability to photoinitiate polymerization of macromolecules that are covalently linked to the surface independent of its bulk chemistry.

Alternatively, reinitiation by activation of DTC-containing surfaces in the presence of a monomer mixture composed of multivinyl monomers and additional initiator facilitates covalent adhesion between adjacent crosslinked layers. This process requires that the rate of surface initiation is rapid enough, relative to the bulk polymerization, to generate sufficient covalent linkages to the previous layer prior to complete curing of the new layer. Qualitative tests of adhesion strength and comparative observations of laminated films, cured in the presence or absence of TED and placed in solvents, provide evidence that the LRPP chemistry imparts strong adhesion (*i.e.* covalent bonds) between adjacent layers.

Step 2 (from Fig. 1) depicts the photolithography procedure

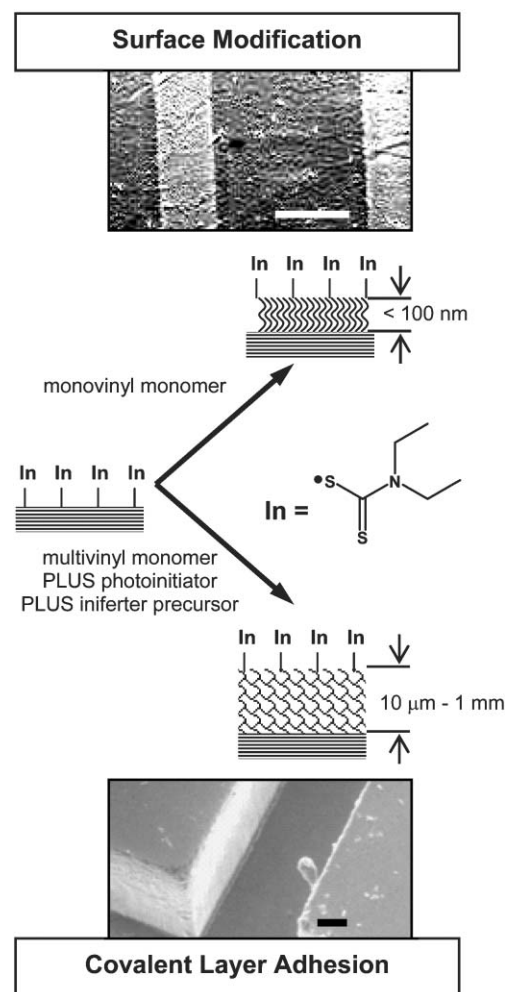


Fig. 2 Photoiniferter chemistry for surface modification and adjacent layer adhesion. Initiation of an iniferter-containing surface in the presence of a pure monovinyl monomer yields polymer grafted to the surface (top route). The dark color reveals a thin hydrophilic film that is covalently bound in a photolithographically-defined pattern to a hydrophobic polymer network surface. Alternatively, exposure of a mixture of a multifunctional monomer, photoinitiator, and photoiniferter precursor on an iniferter-containing surface results in a covalently-adhered layer of crosslinked polymer (bottom route). Scale bars, 100 μm .

used to pattern individual layers that is highly compatible with existing equipment and microfabrication strategies. Generally, masks are made from commercially available emulsion films with a high resolution plotter. The masks are made quickly and inexpensively for rapid prototyping and device optimization. Resolution is *ca.* 10 μm with this method, which is typically sufficient for microfluidic device applications that have characteristic length scales on the order of 100 μm . If necessary, higher resolution (*i.e.* less than 1 μm) and/or more durable masks can be fabricated readily by deposition of chrome on etched quartz glass or alternative printing methods.⁴⁸ Masks are aligned using registration marks and an optical alignment system. The liquid monomer formulation is polymerized by free radical chain polymerization upon flood exposure to 365 nm radiation.

The space between the contacting photomask and the previous layer dictates the height of the current layer. The layer height is controlled through micromanipulators with 1 to 5 μm resolution and a range of 10 μm to 5 mm. The ability to fabricate layers with a wide range of thicknesses translates into fully three-dimensionally controllable microfluidic systems with high aspect ratios (*i.e.* much greater than 10 in many cases).

Step 3 illustrates removal of monomer, which is unreacted

due to masking, by solvent rinsing. This process is analogous to negative photoresist chemistry; unexposed regions are removed and exposed regions remain after solvent rinsing. Any number of monomer formulations are polymerizable sequentially in distinct layers or within each layer, which leads to intralayer functionality unmatched by other fabrication techniques. To fabricate multiple layers with complex undercut geometries, the resulting trenches are filled with a molten wax. The sequence of materials selection, photolithography, and layer preparation is repeated for each layer of the device. Finally, upon completion of the layers, the device is heated to melt the wax in void regions and rinsed with a solvent to remove all wax from the device. The use of sacrificial materials to maintain void regions during subsequent layer polymerization enables fabrication of designs that take advantage of the third dimension in space. However, the devices must be designed to facilitate complete removal of the molten wax upon completion.

The pictures in Step 4 show a cogwheel that was fabricated from five layers. The brown material is wax that was used to planarize each layer prior to depositing additional monomer. After removal of the wax, the cogwheel spins around a solid axle when a fluid (colored blue for visualization) is pumped through the channel on the left side. The pictures show an air bubble deforming as the wheel spins in the cavity. The fluid-driven cogwheel demonstrates the ability of the CLiPP process to generate complex microdevice structures. The set of masks required to fabricate the cogwheel is shown in the supplementary information available on the publisher website.[†]

Fig. 3 depicts selected stages in the CLiPP process to fabricate high aspect ratio structures in a massively parallel fashion. The center image (a) shows a wax-encased 20×20 matrix of University of Colorado buffalo logos elevated on cross-shaped pedestals (b). The images on the right show the intersections of four pedestal bases (c), the cross-shaped pedestals (d) and the same level after filling with molten wax prior to photolithographic polymerization of the buffalo logo

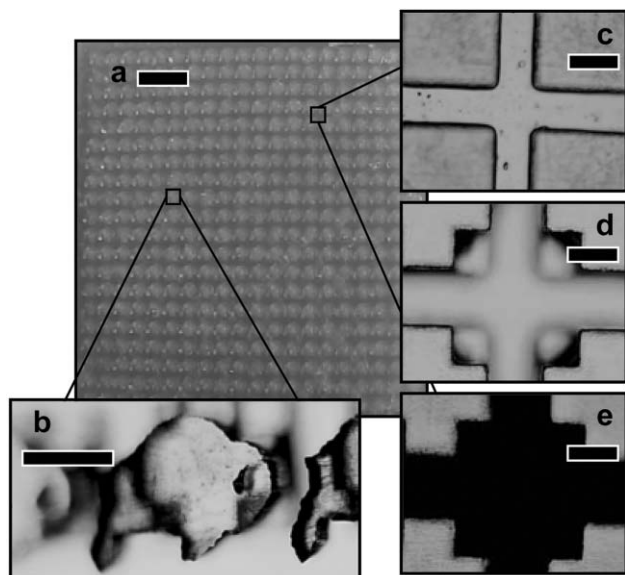


Fig. 3 “Buffalo Herd.” 400 microscale, three-dimensional Colorado buffalo logos on pedestals are constructed in three layers to demonstrate the applicability of the CLiPP process to massively parallel fabrication. (a) The main picture shows the structures prior to release from the sacrificial wax encasement. (b) A single buffalo is shown in the bottom image. The images on the right show the intersections of: (c) four pedestal bases, (d) the cross-shaped pedestals, and (e) the same level after filling with molten wax prior to photolithographic polymerization of the CU buffalo logo. The completed 400-buffalo matrix yields *ca.* 99% unblemished pieces. Scale bars: (a) 3 mm; (b)–(e) 300 μm .

(e). Each buffalo has an overall aspect ratio of *ca.* 0.5 and the 400-buffalo matrix yields *ca.* 99% unblemished pieces.

Fig. 4 contains images of devices that exemplify some of the novel and desirable attributes of microdevices made using the CLiPP process. For example, Fig. 4a contains images of microfluidic components. A device with intertwined channels in multiple layers demonstrates fabrication of complex structures that could enable compact organization of multiple independent fluid streams. Additionally, CLiPP facilitates *in situ* fabrication of ports for external connections. Each port is covalently bound to the device surface and designed to fit 3/32 inch ID tubing in this case.

Fig. 4b contains examples of CLiPP-fabricated devices for biological applications. The image on the left is an example of ten identical cell culture well arrays coupled to a commercially available 5 μm poly(vinylidene fluoride) (PVDF) filter for use in perfusion flow liver cell tissue engineering experiments.⁴⁹ The arrays of 300 μm wells were produced for a fraction of the cost of traditional micromachining methods in glass or silicon. A typical polymer material used for channel structures allows non-specific protein binding and subsequent attachment and survival of fibroblasts (a common mammalian cell type).

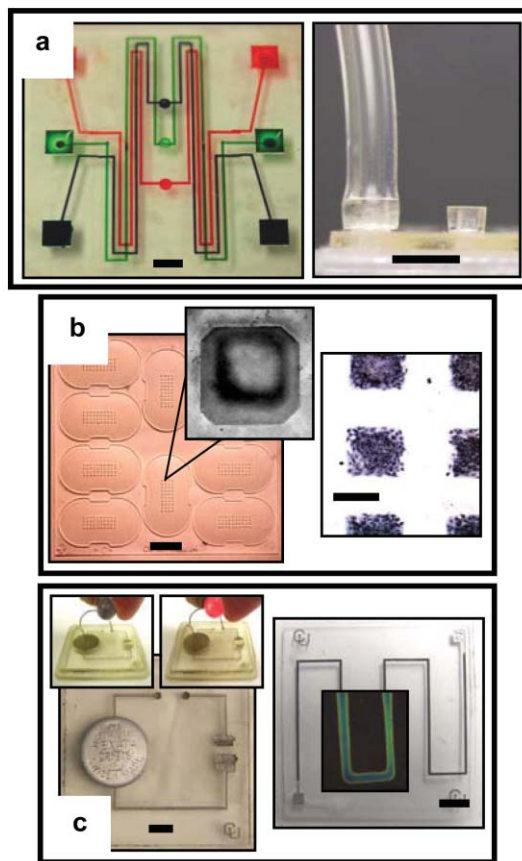


Fig. 4 Pictures of devices fabricated by the CLiPP process. (a) *Microfluidics*. A device with intertwined channels in multiple layers demonstrates fabrication of complex structures (left). External connections are facilitated by covalently attached tubing ports fabricated *in situ* (right). (b) *Biocompatible materials* (left). A custom-designed array of liver cell culture microwells is fabricated directly onto a 5 μm PVDF filter. Furthermore, cells attach and survive on the polymer network used to fabricate structures, but cell adhesion is readily prevented (white regions) by patterning PEG with LRPP (right). (c) *Materials diversity* (left). An electrical switch on a microfluidic device is activated by filling the fluid reservoir with an electrolyte solution. A photopolymerizable carbon filament (right) is incorporated within a two-layer device. The thermotropic liquid crystal film in the overlaid picture indicates spatially-resolved heating of the device surface. Scale bars: (a) 5 mm; (b) (left) 5 mm; (b) (right) 200 μm ; (c) 5 mm.

However, methacrylated poly(ethylene glycol), which is readily patterned by the living radical photopolymerization described in Fig. 2, prevents protein adhesion and cell attachment. In the image on the right of Fig. 4b, the white areas are regions where PEG was grafted to the network surface prior to cell seeding.

One of the main advantages of the CLiPP process is the ability to incorporate multiple types of materials into a single device or into a single layer within a device. The image on the left in Fig. 4c shows a device that incorporates a polymerizable, conductive, silver paste within a crosslinked network that has voids for a battery and an analyte fluid reservoir. Likewise, the image on the right shows a device that contains a conductive carbon filament, which provides heating when a voltage is applied. A thermotropic liquid crystal film reveals the spatial resolution of the heating (e.g. up to 90 °C with an application of 115 V in the device shown). Well-defined temperature zones, in conjunction with fluid channels, are necessary for thermal cycling operations used for amplification of genomic information (e.g. microPCR⁵⁰), and other applications.

Conclusions

A new approach for the construction of polymeric micro-devices was introduced. Contact Liquid Photolithographic Polymerization (CLiPP), enables fabrication of geometrically and functionally complex devices *via* unique photoinitiation chemistry in conjunction with liquid monomers enclosed within custom-designed mask aligner tooling. Examples of micro-devices fabricated with CLiPP illustrate the advantages over other microfabrication technologies, which include facile surface modification, and incorporation of different functional materials within one or more covalently-bound layers.

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