Narrative Progress Report
PRF#: 59067-DNI7
Project Title: Colloidal Rotaxanes: Polymer Particles With Mechanical Bonds
P.I. Name & Affiliation: Carson Bruns, ATLAS Institute, Department of Mechanical Engineering, University of Colorado Boulder, 1125 18th St., UCB 320, Boulder, CO 80309

Project Goals. The goal of the ACS PRF DNI project 59067-DNI7, titled "Colloidal Rotaxanes: Polymer Particles With Mechanical Bonds", is to develop a new class of colloids comprising suspensions of mechanically interlocked microparticles. We aim to create mechanical entanglements between polymer particles by generating size- and shape-complementary micro-hydrogels that self-assemble into threaded / interpenetrated structures akin to rotaxane molecules. We proposed to build a stop-flow lithography (SFL) apparatus for the rapid synthesis of these uniform-size/shape micro-hydrogels. We further proposed to incorporate hydrophobic & hydrophilic or positive & negative charged moieties into the hydrogel networks in order to guide their interpenetrative self-assembly. Upon completion of the project, we expect this SFL device to enable the generation of the first self-assembled "colloidal rotaxanes" in high throughput.

Current Progress. The project is being carried out in to two phases. Phase I (Year 1) involves building and optimizing a stop-flow lithography (SFL) apparatus for the high-throughput synthesis of uniform, shape-defined micro-hydrogels. Phase II (Year 2) involves using this device to generate rod-shaped and donut-shaped micro-hydrogels and facilitating their self-assembly into ring-on-a-string structures. We begin Year 2 of the project on schedule, in transition from Phase I to II.

Phase I. Stop-Flow Lithography Apparatus
Through the concerted effort of several team members, we have successfully constructed a custom-built stop-flow lithography (SFL) apparatus (**Figure 1**). We programmed an Arduino device to actuate the shutter and the solenoid valve that control the photo-polymerization and flow, respectively, within the microfluidic devices where our micro-hydrogels will be made.

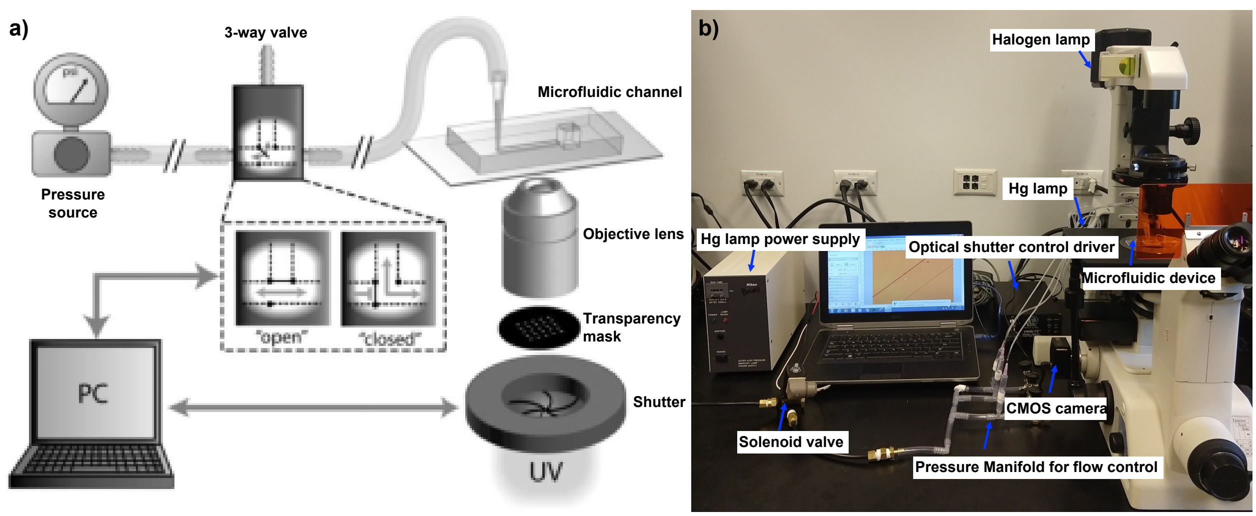

Figure 1. Diagram (a) and photograph (b) of our in-house stop-flow lithography device.

After building the SFL apparatus, we have been optimizing the microfluidic component. We employ standard SU-8 photolithography techniques to generate microfluidic devices of the kind represented in **Figure 2a-b**.

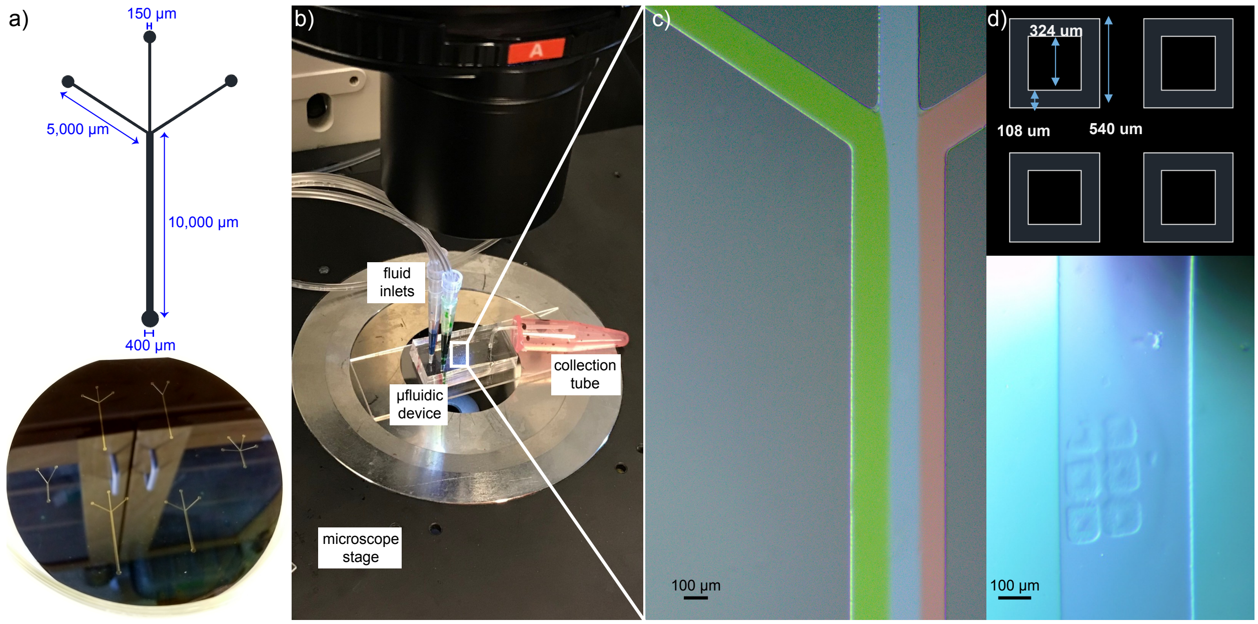

Figure 2. Microfluidic component of SFL apparatus. (a) Diagram and photograph of microfluidic device design on SU-8 photoresist. (b) Photograph of microfluidic device in SFL. (c) Optical micrograph of three-channel laminar flow in a device. (d) Diagram of transparency mask and photograph of square-shaped micro-hydrogels synthesized in-house by SFL.

We have thus far demonstrated that we can achieve three-channel laminar flow (**Figure 2c**) in our microfluidic channel by adding green, blue, and red dyes to the fluids in each channel. With acrylic monomers in the fluids, we have shown that sub-second intervals of UV exposure through a transparency mask generates shape-defined micro-hydrogels (**Figure 2d**) in the device.

Future Work. Currently, we often observe clogging and blurry shapes, so Year 2 of the project will involve further optimization of micro-hydrogel synthesis, as well as its application to the self-assembly of interpenetrated microparticles.

Phase II. Self-Assembly of Colloidal Rotaxanes
We will use our SFL machine to generate "ring" and "rod" microparticles comprising, e.g., positively and negatively charged hydrogels, respectively. We expect that we can optimize the size- and shape-complementarity of these particles such that they minimize their energy by self-assembling into interpenetrated "ring-on-a-rod" structures. Successful completion of the project would entail orchestrating this self-assembly by mixing the particles in a fluid, and writing our first publication describing the successful formation of these "colloidal rotaxanes".

Impact of the research on personnel. The majority of funds have been used to support postdoctoral researcher Hyejin Kwon. The project has enabled Dr. Kwon to learn a variety of new skills in photolithography, optics, device engineering, and microfluidics, diversifying her expertise and widening her options for her future career.

Impact of the research on PI's career. This work will clearly have a significant and lasting positive impact on the PI's career. The SFL device, built with PRF support, gives the PI's laboratory a new niche; a unique capability that will drive not only the proposed research, but also a wealth of future projects and collaborations. The results we are obtaining now will also leave the PI well-positioned to apply for larger grants (e.g., NSF polymer, particulate and multiphase processes, or materials divisions) extending from this foundational work.