

# Microfluidic Combinatorial Polymer Research\*

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## INTRODUCTION

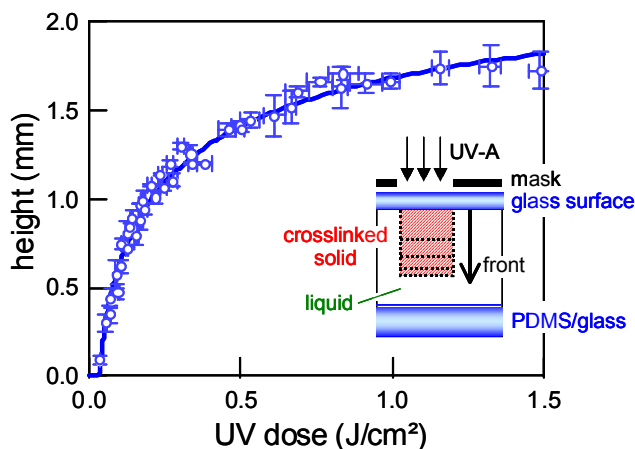
Meeting an increasing demand for combinatorial studies in polymer formulations, we explore microfluidics as a high throughput research tool. Although well established in biology and analytical chemistry, few applications of microfluidics exist in polymer science, due in part to limited device chemical compatibility. However, the small sample volumes (typically  $\mu\text{l}$ ) required, the device size (and cost) reduction and the superior measurement speed of this methodology are definite driving forces for a polymer research commitment to microfluidics.

A key goal for polymer formulation research is the elucidation of the relationship between specialty polymers and complex fluid behavior. To this end, we design fluidic modules (sample preparation and mixing units, component synthesis and measurement devices) in which dynamic mixture libraries are created and their properties monitored and quantified *in situ*. This requires a new paradigm in which polymer synthesis is carried out concurrently to characterization, manipulation and complex measurement methods, on a scale compatible with this miniaturized combinatorial platform.

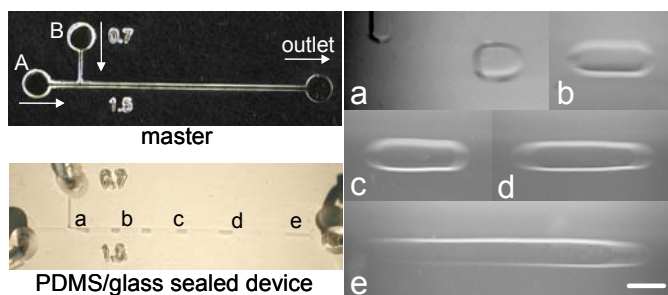
In this preprint, we review three microfluidics initiatives in the Polymers Division at NIST: (a) device fabrication compatible with polymer formulations, (b) measurements in immiscible fluid droplets and (c) polymer synthesis in microchannels.

## DEVICE FABRICATION

We have recently reported on a rapid prototyping technique capable of fabricating tall, solvent-compatible fluid handling devices.<sup>1,2</sup> This method consists of contact lithography of multifunctional thiolene-based adhesives, using a collimated UV-A source and a printed transparency as photomask (designed with a standard graphics package). The high UV absorption and limited mass transfer yield an accurately controlled frontal photopolymerization reaction.<sup>2</sup> The front position as a function of UV dose for one photoresist is shown in



**Figure 1.** Height dependence on the UV dose during the frontal photopolymerization of a multifunctional polymer resist<sup>2</sup> (the standard uncertainty in height and dose is 5 and 4 %, respectively). The solid line is a model<sup>2</sup> fit to the data. The insert depicts a schematic of the rapid prototyping method, showing a photomask, top and bottom confining surfaces and solid/liquid front propagation in the resist.



**Figure 2.** T-channel master and PDMS glass-sealed replica (open-faced procedure) with a height gradient along the main channel. As a result, a water input *B* plug in silicone oil (input *A*, contrast matched to the device) becomes extended several times its original length near the exit. The scale bar is 500  $\mu\text{m}$ .

figure 1. While the vertical dimensions are determined by the UV dose (in a continuous fashion, in contrast with discrete spin casting), the lateral dimensions are determined by the photomask. Typical fluid channels have a 400  $\mu\text{m}$   $\times$  400  $\mu\text{m}$  cross-section, but a range of dimensions are possible. In fact, one major asset of this technique is the ability to pattern mm-tall structures on glass, which would be demanding (or impossible) for conventional lithographic techniques. Another is the solvent resistance of the crosslinked matrix to a range of organic solvents (in contrast, PMDS devices are mainly limited to aqueous applications).

Solvent resistant devices are fabricated by confining the liquid resist between two glass plates (figure 1), with a gasket between them, and crosslinking its full depth through a photomask. The illuminated portions solidify (these are negative photoresists) while the masked regions remain liquid and can be washed away with selective solvents (ethanol and acetone). Devices of this kind are used for polymerization in microchannels, as described in the last section of this preprint. In addition, free standing devices, completely made of the crosslinked resin, can be fabricated using sacrificial substrates and taking advantage of the frontal nature of the reaction.

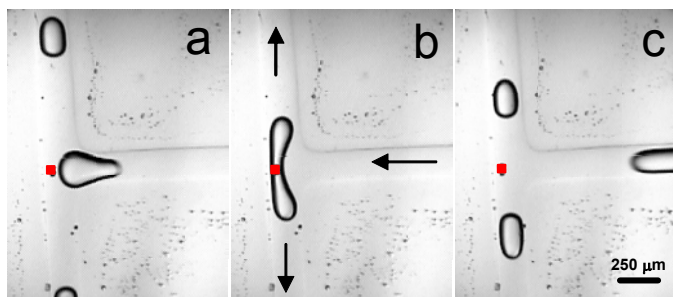
Poly(dimethyl siloxane) (PDMS) devices are promptly fabricated with an alternative protocol. It consists of using a relief bottom surface (crosslinked PDMS) while patterning the resist and selective washing of uncrosslinked material, resulting in a patterned thiolene *master* on glass. This (reusable) master can be replicated onto PDMS which can then be sealed irreversibly against glass, after a simple surface treatment of both contact surfaces.<sup>1,3</sup> An example of such procedure is given in figure 2, where a master and a PDMS replica are shown (left panels). This T-channel configuration has a linear height gradient running from left (800  $\mu\text{m}$ ) to right (100  $\mu\text{m}$ ), demonstrating an additional capability of this prototyping technique: to generate non-planar structures by resist confinement (or multistep imaging<sup>2</sup>). This topography results in a velocity gradient along the channel. An immiscible oil/water flow, producing water plugs at the T-junction, is employed to demonstrate an over 10-fold increase in plug length. Both methodologies,<sup>1</sup> close-faced (all enclosed resin matrix) and open-faced (PDMS replication) allow easy input/output connections to fluid pumps and reservoirs. However, the latter is more amenable to the inclusion of simple valves and pumps.<sup>4</sup>

The following section expands on immiscible fluid flow manipulation (using open-faced devices) with an emphasis on measuring relevant fluid properties. We then report on preliminary polymerization experiments (using close-faced devices) in fluidic handling devices. The last section concludes the paper.

## HIGH-THROUGHPUT MEASUREMENTS OF IMMISCIBLE FLUIDS

Droplet formation<sup>5,6</sup> and breakup<sup>7</sup> have received considerable attention due to the complexity of patterns formed in microfluidic geometries. In addition, efficient mixing inside droplets with no dispersion has been demonstrated in tortuous channels, even at low Reynolds numbers.<sup>8,7</sup>

Building on droplet breakup studies occurring at an inverted T-junction,<sup>7</sup> we explore high-throughput strategies to measure physical properties, including the interfacial tension between two fluids. Figure 3 shows a sequence of images of a water plug in a silicone oil matrix phase extending and eventually breaking at the stagnation point (red square) of an inverted T-junction. By determining the degree of drop deformation and the breakup threshold (determined by capillary stability conditions), the interfacial tension between the liquids can be estimated (other parameters can be determined separately). Other strategies of deforming droplets and following their subsequent relaxation include active flow field manipulation in a versatile cross-flow device, providing access to a remarkably large window of flow types (extension, shear and rotation).<sup>9</sup> These devices take advantage of an online image analysis feedback controlling volume-displacement liquid pumps but require a fast device response which can be obtained by an appropriate choice of geometry and fabrication. A four-roll mill microfluidic analog has recently been demonstrated by Hudson *et al.*<sup>9</sup>

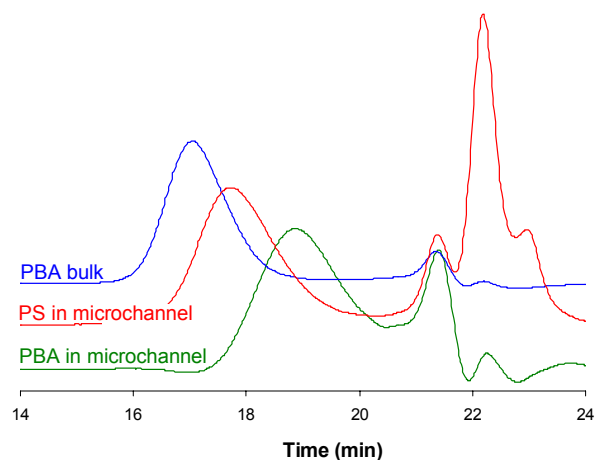


**Figure 3.** Droplet (water in silicone oil) breakup at an inverted T-junction. The arrows indicate the flow directions and the solid square marks the stagnation point in the flow field. Break-up is determined by droplet size, velocity, liquid viscosities and interfacial tension.<sup>7</sup>

#### POLYMER SYNTHESIS IN MICROFLUIDIC DEVICES

One of the most sensitive and widely varied parameters in compatibilizing two immiscible fluids is the composition of the compatibilizers used. These polymers are typically well-defined in both comonomer composition as well as molecular mass,  $M_r$ . Recent advances in polymer chemistry have vastly expanded the range of both of these variables in specialty additives.<sup>10</sup> As a demonstration of the potential to change one of these variables in a microfluidic channel and, eventually, on-a-chip, we have carried out controlled radical synthesis of homopolymers in a microfluidic device (close-faced on glass). By varying the flow rate of a reaction solution through a temperature controlled channel of fixed length, we were able to change the resultant molecular mass of the polymer output.<sup>11</sup>

As shown in figure 4, we were able to produce polystyrene and poly(n-butyl acrylate) with narrow polydispersity and controlled molecular mass, where flow rate could be tied to the reaction time and, therefore, the conversion of monomer in a polymerization. Future work includes the introduction of comonomers into the reaction mixtures and the integration of the temporally varying polymer outputs with the high throughput measurements of flow behavior in immiscible polymer solutions.



**Figure 4.** Gel permeation chromatography (GPC) traces of two homopolymers, poly(styrene) and poly(n-butyl acrylate), polymerized in a long serpentine solvent resistant microchannel (500 x 500  $\mu\text{m}^2$  cross-section).<sup>11</sup> The standard measurement uncertainty is less than 5 %. A trace of solution polymerization of PBA is shown for comparison.

#### SUMMARY

We have demonstrated that versatile fluid handling devices, compatible with an array of organic solvents relevant to polymer research, could be fabricated using a novel rapid prototyping technique.<sup>1,2</sup> The device design, fabrication (and possible replication) and inlet/outlet connections take only a few hours, which allows for quick iterations and performance optimization. Active and passive flow field control has been investigated in the context of immiscible flows. A number of strategies were developed to measure relevant fluid properties, including interfacial tension. Finally, we demonstrated that controlled homopolymer polymerization could be carried out in microfluidic channels. At present, we are integrating these various modules in a comprehensive combinatorial tool for polymer formulations research.

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