

# Living anionic polymerization using a microfluidic reactor

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Received 12th June 2008, Accepted 22nd September 2008

First published on the web 28th October 2008

Living anionic polymerizations were conducted within aluminum-polyimide microfluidic devices. Polymerizations of styrene in cyclohexane were carried out at various conditions, including elevated temperature (60 °C) and high monomer concentration (42%, by volume). The reactions were safely maintained at a controlled temperature at all points in the reactor. Conducting these reactions in a batch reactor results in uncontrolled heat generation with potentially dangerous rises in pressure. Moreover, the microfluidic nature of these devices allows for flexible 2D designing of the flow channel. Four flow designs were examined (straight, periodically pinched, obtuse zigzag, and acute zigzag channels). The ability to use the channel pattern to increase the level of mixing throughout the reactor was evaluated. When moderately high molecular mass polymers with increased viscosity were made, the patterned channels produced polymers with narrower PDI, indicating that passive mixing arising from the channel design is improving the reaction conditions.

## Introduction

Microscale flow reactors are increasingly being used to carry out chemical reactions,<sup>1</sup> including polymerizations.<sup>2,3</sup> Microchannel reactors differ from conventional batch reactors in primarily two ways. Heat transfer is greatly accelerated, especially when the reactor is made of materials that conduct heat well (*e.g.*, metal). In addition, the narrow dimensions of the channel often result in laminar flow with reagent mixing limited only to diffusion, although the flow design often can be modified to obtain increased mixing.<sup>4</sup> Examples of mixing strategies include an interdigitated slit micromixing unit developed at the Institut für Mikrotechnik Mainz (IMM),<sup>5</sup> segmented reaction droplets,<sup>6–8</sup> and patterned mixing channels for continuous passive mixing.<sup>9–11</sup> The unique features of microreactors have been found to increase the yield and selectivity for organic syntheses,<sup>12,13</sup> and narrow the molecular mass distribution for polymerizations.<sup>14</sup> Distinct from the direct impact on synthesis, there are other advantages, such as reducing reagent consumption, simplified automation for high throughput screening,<sup>15</sup> and integration of synthetic processes with analysis techniques (*i.e.*, micro-total analysis systems).<sup>16,17</sup>

Living anionic polymerization is well suited for microchannel synthesis because it is exothermic (*e.g.*, the enthalpy of polymerization for styrene is  $\Delta H = -73$  kJ/mol), and rapid rates of polymerization require efficient heat dissipation to maintain a controlled temperature. Living anionic polymerization under flow conditions was initially demonstrated by Swarc.<sup>18–20</sup> These studies polymerized styrene in tetrahydrofuran

(THF) at room temperature, which resulted in polymerizations reaching full conversion in less than 1 s. By conducting the reactions in 1 mm glass capillaries, reaction times as short as 80 ms could be probed while maintaining a constant reaction temperature. The authors noted that as long as they maintained high flow rates, the reagents were sufficiently mixed.

Recently, several groups have examined polymerizations within narrow continuous flow tubing reactors. Much of this work has made use of the IMM micromixing units connected to stainless steel tubing reactors.<sup>21–23</sup> The micromixer geometry combines reagents in thin layers (<50  $\mu\text{m}$ ) allowing for mixing in as little as a few ms, and has been observed in some cases to have better mixing than turbine mixers. They have been demonstrated on several fast, exothermic polymerizations. Yoshida and coworkers have used IMM microreactors to conduct cationic polymerization of vinyl ethers<sup>24</sup> and diisopropylbenzenes.<sup>25</sup> They have also used the microreactors to conduct free radical polymerizations initiated by azobis(isobutyronitrile) (AIBN).<sup>26</sup> In all cases they obtained narrower polydispersities than batch polymerizations. In the case of cationic polymerization, improvement was attributed to fast mixing, whereas in the free radical polymerizations it was attributed to improved heat transfer. Recently, a glass tube reactor was used to conduct photo-initiated free radical polymerization of *n*-butyl acrylate.<sup>27</sup> Atom transfer radical polymerizations (ATRP) and amino acid polymerizations have also been conducted within Teflon tubing reactors.<sup>28,29</sup> In addition, nitroxide mediated radical polymerization (NMRP) has been conducted within a stainless steel tubing reactor.<sup>30</sup> Moreover, Frey and coworkers have provided an excellent review of microreactor polymerizations, and very recently reported results of living anionic polymerization within IMM microreactors.<sup>3,31</sup> Also, Yoshida and coworkers have very recently described anionic polymerization of styrene derivatives within IMM microreactors.<sup>32</sup>

Polymerizations have also been conducted within conventional (*e.g.*, polydimethyl siloxane)<sup>33</sup> microfluidic devices. Much of this work has harnessed flow focusing to produce droplet reactors suspended or segmented by an immiscible water or oil phase. In the case of segmented flow, the mixing improves and axial dispersion decreases.<sup>34</sup> In the case of suspended droplets, viscosity concerns are eliminated, and the droplets are often solidified, for example by photo-initiated free radical polymerization. Flow designs allow for complex polymeric particles to be prepared as small as 75  $\mu\text{m}$ .<sup>35,36</sup>

For the past several years, our group has approached the concept of microreactors from the standpoint of creating a micro-total analysis system ( $\mu\text{TAS}$ ).<sup>15</sup> During this time we have evaluated the integration of small angle light scattering,<sup>37</sup> Raman spectroscopy,<sup>38</sup> and recently dynamic light scattering<sup>39</sup> onto microfluidic platforms. The microfluidic reactor, therefore, was used as a means of providing samples to these analytical tools in a high throughput manner. As such, we employed atom transfer radical polymerization (ATRP), even though it did not require rapid heat dissipation or high speed mixing. The main advantage of ATRP was its generality in controlling polymerization of a variety of monomers. On the other hand, ATRP does embody many of the challenges associated with conducting polymerizations within microreactors, including prolonged use of hot organic solvents and elevated viscosity. In dealing with these challenges we developed a simple low cost aluminum-Kapton microfluidic device well suited for conducting various ATRPs.

In this paper, we evaluate the performance of this type of aluminum-Kapton microfluidic device in carrying out living anionic polymerizations. Like the stainless steel IMM microreactors, these devices have the ability to rapidly dissipate heat from fast exothermic reactions, thereby preventing uncontrolled heating. Polymerizations of styrene in cyclohexane are carried out at elevated temperature and monomer concentrations to highlight the ability of the devices to dissipate heat even from these more demanding conditions. In addition, the channels within these devices can be designed with various two-dimensional patterns. Four types of channel design are compared to determine how adjustment of flow patterns can enhance the performance of the microreactor.

## Experimental

### Materials

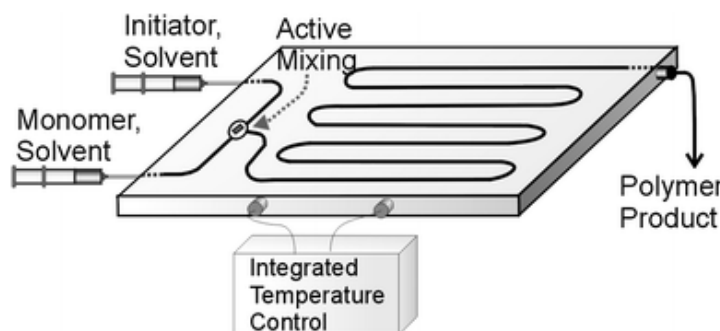
*sec*-Butyl lithium (*s*-BuLi, 1.4 mol/L solution in cyclohexane) and cyclohexane (anhydrous, 99.5%) were purchased from Aldrich,<sup>40</sup> and used as received. *s*-BuLi was titrated by the standard titration method using diphenylacetic acid described in the literature.<sup>41</sup> The observed concentration of *s*-BuLi was 1.03 mol/L. Styrene and isoprene were purchased from Aldrich. Styrene was washed with NaOH to remove the inhibitor and distilled from  $\text{CaH}_2$  under reduced pressure. Isoprene was distilled from  $\text{CaH}_2$ .

## Characterization

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  as a solvent on a JEOL 270 MHz spectrometer and were reported in parts per million ( $\delta$ ) from an internal tetramethylsilane (TMS) or residual solvent peak. The number averaged molecular mass ( $M_n$ ) and polydispersity index: PDI ( $= M_w/M_n$ ) of polymers were determined by a size exclusion chromatography (SEC) instrument described elsewhere.<sup>39</sup> The columns were calibrated by a series of polystyrene standards (Polymer laboratories, EasiCal PS-2) at 40 °C in tetrahydrofuran (THF, flow rate; 1.0 mL/min).

## Example protocol for styrene polymerization

Two reagent solutions were prepared and separately introduced into the microfluidic device as is depicted in [Fig. 1](#). **Initiator Solution:** A cyclohexane solution of *s*-BuLi (1.03 mol/L, 0.8 mL) was diluted with anhydrous cyclohexane (9.2 mL) under an Argon atmosphere. This solution (0.083 mol/L *s*-BuLi) was gently degassed with Argon for 5 min, and withdrawn into a 10 mL glass syringe. **Monomer Solution:** Styrene (8.7 mol/L, 5 mL) was diluted with anhydrous cyclohexane (5.0 mL) and the solution (4.35 mol/L, St) was gently degassed with argon for 5 min, and withdrawn into a 10 mL glass syringe. The two syringes were mounted on syringe pumps (Braintree Scientific),<sup>40</sup> and connected to a microfluidic reactor with Teflon tubes (I.D. = 790  $\mu\text{m}$ , O.D. = 1.58 mm). The products obtained from the polymerizations were collected from the outlet (*ca.* 200  $\mu\text{L}$ ), and dissolved in Argon-purged THF containing methanol (*ca.* 5% by volume) to terminate the polymerization. The crude solution was measured by  $^1\text{H}$  NMR and SEC to determine the conversion of monomer, number-averaged molecular mass ( $M_n$ ), and polydispersity index (PDI) of polymers.<sup>42</sup> All of the reactor components, including the syringes and fittings, were used only after being rinsed with THF and acetone, dried at 105 °C for at least 1 h, and stored under vacuum in a desiccator. In addition, the initiator solution (*ca.* 1 mL) was flowed through the device immediately preceding the polymerization to react with any trace impurities.

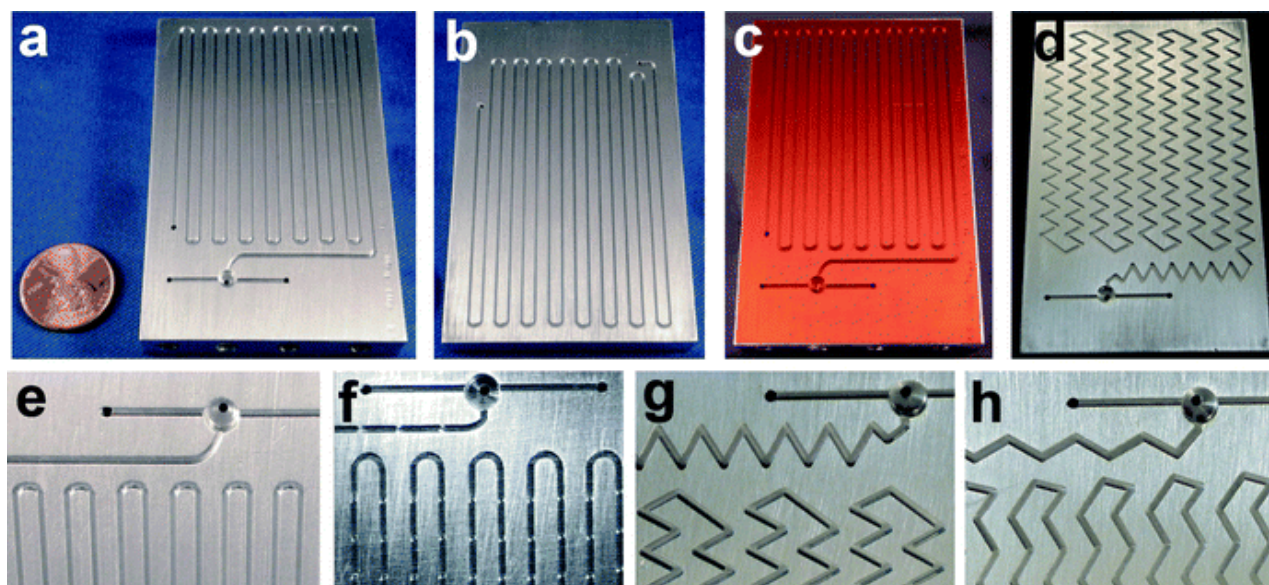


**Fig. 1** Schematic of living anionic polymerization using a microfluidic reactor.

## Design of microfluidic reactors

Our microfluidic reactors are described in more detail in a previous report from our group.<sup>39</sup> Our microfluidic reactors consist of channels machined into an aluminum plate (7.6 cm  $\times$  5.0 cm  $\times$  1.0 cm) pretreated using plasma oxidation ([Fig. 2a](#)). The microchannels (rectangular cross section of 790  $\mu\text{m}$  wide and 500  $\mu\text{m}$  deep, and *ca.* 2 m length) are cut into on both sides with standard machine bits (790  $\mu\text{m}$  diameter solid carbide endmill McMaster Carr 8795A121) and sealed by attaching Kapton film (130  $\mu\text{m}$  inch thickness) to the aluminum surface with chemically resistant epoxy (Master Bond EP41S-4).<sup>41</sup> This Kapton film can be stiffened by gluing a second layer on top of it. Since the polymer solutions possessed a somewhat high viscosity, the channel dimensions were not reduced to dimensions often associated with microfluidic channels. Narrower channels can be produced by mechanical machining, although production of increasingly narrow channels can make the procedure become challenging. Production of channels in this way allows for flexibility in creating channel patterns. In this work, four different channel designs were produced, as is shown in [Fig. 2e–h](#). The design patterns are aimed at enhancing mixing along the length of

the channel. Initial mixing of the reagents, however, is completed in a 14  $\mu\text{L}$  well with an active mixing element. The stirring rate (*ca.* 2 Hz) was sufficiently fast to ensure proper mixing at all the examined flow rates. Stable temperatures ( $\pm 0.3$   $^{\circ}\text{C}$ ) are maintained by integrating a thermocouple and heating cartridges directly into the center of the devices. Occasional plugs in the channels are cleaned out after removing the Kapton, and then replacing it. As noted in our previous work, the devices are simple and inexpensive to prepare, and standard HPLC fittings are used to assemble the system.<sup>39</sup> One concern with aluminum reactors is their potential for reactivity. For example, it is well known that aluminum and aluminum oxide react with aqueous hydroxide anions. In our work, however, we did not find any evidence of the carbanions reacting with the aluminum. However, if the reactivity of the aluminum is problematic, an alternative substrate such as stainless steel could be used.



**Fig. 2** (a) Machined aluminum plate, top side, (b) back side of microfluidic device, (c) microreactor sealed with polyimide film, (d) microfluidic reactor with zigzag pattern. Also shown are close up views of (e) straight channel, (f) straight channel with periodic pinches, (g) channel periodically bent at acute angles, (h) channel periodically bent at obtuse angles.

## Results and discussion

A key feature of these microfluidic reactors is their ability to efficiently dissipate heat produced by exothermic reactions. The two main factors governing heat generation in a given polymerization are reaction temperature and monomer concentration. Living anionic polymerizations of styrene in cyclohexane are typically conducted at  $\leq 40$   $^{\circ}\text{C}$  and with  $\leq 20\%$  by volume styrene. Batch reactions in excess of these conditions will generate heat faster than can be dissipated, resulting in autoaccelerating increases in reaction temperature. Ultimately, such reactions will boil the cyclohexane, potentially producing dangerous increases in reactor pressure. Due to the stability of the polystyrene anion and the fact that the cyclohexane that remains in liquid form does not heat beyond its boiling point (81  $^{\circ}\text{C}$ ) at ambient pressure, uncontrolled reactions, while dangerous, often produce polymers with PDI values  $\leq 1.1$ . Uncontrolled heating of many other monomer and solvent compositions, however, will result in undesirable side reactions.

[Table 1](#) lists several reactions that highlight the ability of the microfluidic device to carry out living anionic polymerizations, including conditions with elevated temperature and monomer concentrations. Entries 1,2 compare a typical batch reaction with one carried out in a microfluidic reactor. In both cases, a well defined polymer ( $M_n = 5300$  g/mol, PDI  $\leq 1.09$ ) was obtained. Entries 3 and 4 list results for polymerizations conducted at 60  $^{\circ}\text{C}$ . The reactions completed in less than 4 min. Entry 4 corresponds to a

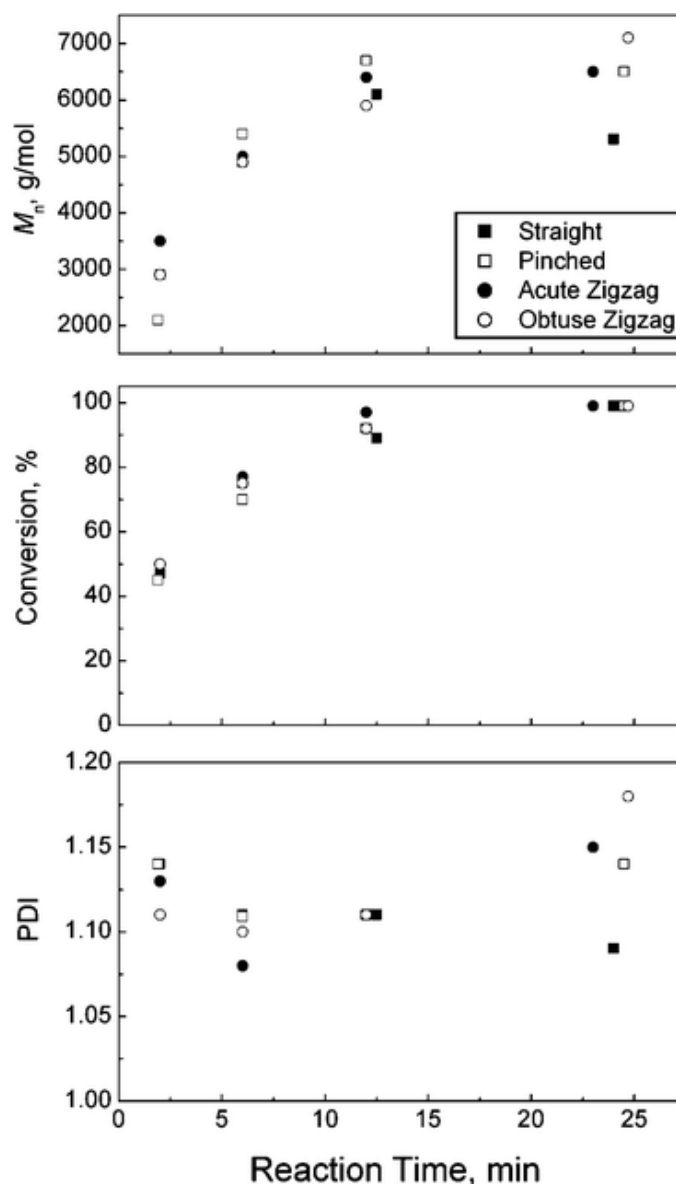
microfluidic device having channels with larger cross section (1.58 mm × 1.58 mm). There was no noticeable impact of this channel size, with both reactors (entries 3,4) producing well defined materials (PDI ≤ 1.12). The combination of elevated temperature and high monomer concentration represent extremes in the rate of heat generation, and these reactions are listed in entries 5,6. Both conditions produced polymer with PDI ≤ 1.19. The transparent Kapton allowed for visual verification that no bubbles were produced under any of these conditions, indicating the reaction temperature never reached the boiling point of cyclohexane (81 °C). Also, the embedded thermocouple did not indicate any rise in temperature. In addition to styrene, an isoprene polymerization is demonstrated (entry 7). Polyisoprene is well suited for microfluidic reactors given its low viscosity and excellent solubility in cyclohexane. Due to the low boiling point of isoprene (34 °C), low reaction temperatures are required, although monomer concentrations as high as 50% by volume were easily polymerized within these microfluidic reactors.

**Table 1** Living anionic polymerization on a straight channel microfluidic reactor

| Entry          | Mon./eq <sup>a</sup> | [St] (Vol %) | [ <i>s</i> -BuLi] (mol/L) <sup>b</sup> | Flow rate (mL/h) <sup>c</sup> | Cond. (°C/min) <sup>d</sup> | Conv. (%) <sup>e</sup> | <i>M</i> <sub>n,SEC</sub> <sup>f</sup> | PDI <sup>f</sup> |
|----------------|----------------------|--------------|--|-------------------------------|-----------------------------|------------------------|--|------------------|
| 1 <sup>g</sup> | St/53                | 25           | —                                      | —                             | 35/25                       | 99                     | 5300                                   | 1.08             |
| 2              | St/53                | 25           | 0.082                                  | 1.0, 1.0                      | 35/24                       | >99                    | 5300                                   | 1.09             |
| 3              | St/53                | 25           | 0.082                                  | 6.0, 6.0                      | 60/4                        | >99                    | 5400                                   | 1.10             |
| 4 <sup>h</sup> | St/53                | 25           | 0.082                                  | 6.0, 6.0                      | 60/25                       | >99                    | 5300                                   | 1.12             |
| 5              | St/64                | 42           | 0.343                                  | 2.0, 10.0                     | 60/4                        | >99                    | 5500                                   | 1.18             |
| 6              | St/106               | 42           | 0.206                                  | 2.0, 10.0                     | 60/4                        | >99                    | 8700                                   | 1.19             |
| 7              | IP/122               | 50           | 0.082                                  | 0.5, 0.5                      | 30/50                       | 91                     | 8300 <sup>i</sup>                      | 1.10             |

<sup>a</sup> Monomer (styrene or isoprene) and equivalents of monomer with respect to initiator. <sup>b</sup> [*s*-BuLi] in the initiator syringe. <sup>c</sup> Pumping rates of syringes with initiator and syringe with monomer, respectively. <sup>d</sup> Reaction conditions including temperature and reaction time. <sup>e</sup> Determined by <sup>1</sup>H NMR analysis of crude samples. <sup>f</sup> Measured by SEC using PS standards. <sup>g</sup> Polymerization was conducted in a glass tube (i.e., batch condition) with [*s*-BuLi] = 0.041 M. <sup>h</sup> Polymerization was conducted microfluidic reactor with larger channels (i.e., 1.5 mm square cross-section). <sup>i</sup> Mismatch with targeted *M*<sub>n</sub> expected to be caused by use of PS GPC calibration.

Beginning with the work of Swarc,<sup>20</sup> it has been clear that flow reactors are useful in evaluating polymerization kinetics. Fig. 3 lists kinetic data for the four different device designs. Comparisons could not be made to batch reactions due to their lack of temperature control. The proportional increase in *M*<sub>n</sub> with respect to conversion indicates the polymerizations proceeded in the microchannels without termination. Under these conditions, however, there was little observed difference in conversion and *M*<sub>n</sub> among the four designs.



**Fig. 3** Plots of  $M_n$ , conversion, and PDI for various reaction times. The total reaction times were determined by adjusting the overall flow rates of reagents. Reaction conditions are: 53 equivalents styrene, 35 °C, 25% by volume of styrene in cyclohexane.

Adjusting the relative flow rates of initiator and monomer allows for simple means of targeting a range of molecular masses. Previous work in our lab has shown, using ATRP, that this concept can be a useful approach to high throughput creation of libraries of materials.<sup>43</sup> Table 2, entries 1–4 list data where various molecular mass polymers were targeted by changing relative flow rates of monomer and initiator. It is noted that this differs from our previous reports where the total flow rate was adjusted to vary the product molecular mass. It is apparent from these data that the observed molecular masses were higher than expected, and that as the targeted molecular mass increased the observed PDI value increased. These reactions are further described with normalized GPC curves in Fig. 4a. Given the sensitivity of living anionic polymerization to trace impurities, such as water, it may be possible that inadequate reagent purification affected the ability to target a given  $M_n$ . Many procedures exist for obtaining higher purity reagents, such as directly distilling cyclohexane from *n*-butyl lithium,<sup>44</sup> and high-vacuum techniques.<sup>45</sup> In

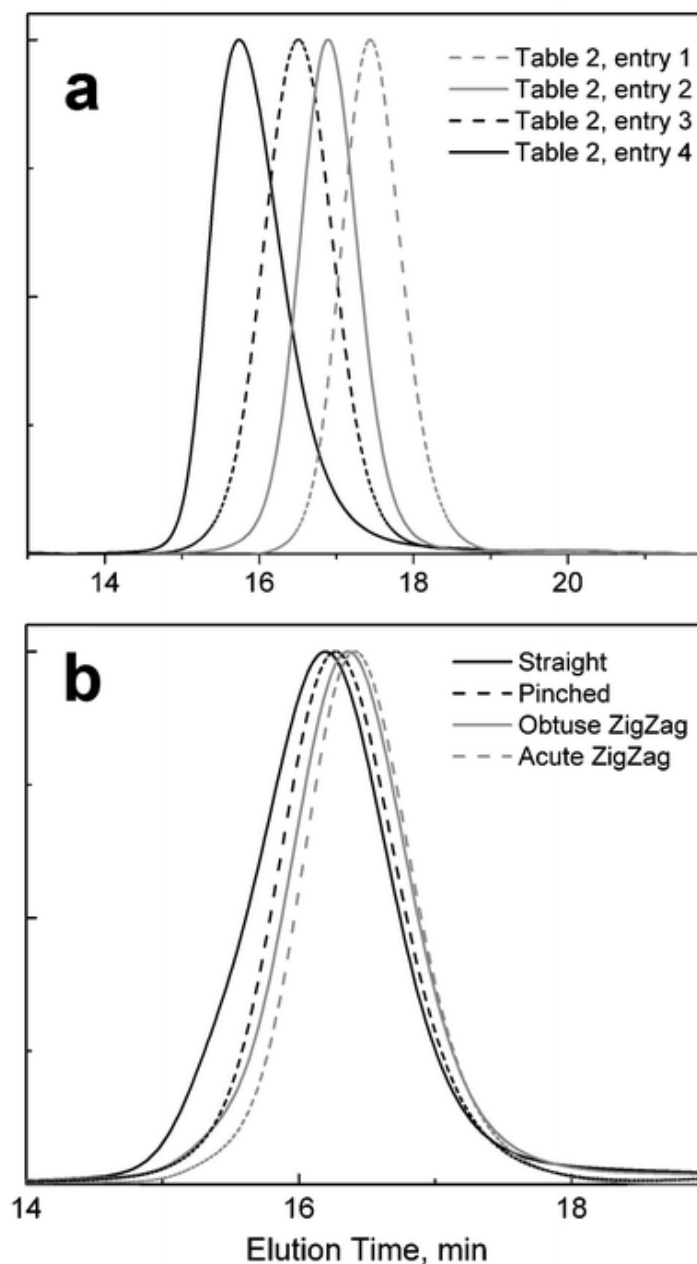
this work, such stringent purification steps were not employed, but these devices can be compatible with several of these procedures. It should be noted that Frey and coworkers have very recently demonstrated the incorporation of some of these purification methods into microreactors.<sup>31</sup>

**Table 2** Living anionic polymerization on microfluidic reactors with various flow rates

| Entry          | Micoreactor   | [St]/[ <i>s</i> -BuLi] <sup>a</sup> | [St] (Vol %) | eq <sup>b</sup> | Rate (mL/h) <sup>c</sup> | Cond. (°C/min) <sup>d</sup> | Conv. (%) <sup>e</sup> | <i>M</i> <sub>n</sub> <sup>f</sup> | PDI <sup>f</sup> |
|----------------|---------------|-------------------------------------|--------------|-----------------|--------------------------|-----------------------------|------------------------|------------------------------------|------------------|
| 1              | straight      | 2.18/0.041                          | 25           | 53              | 2.00, 2.00               | 35/12                       | 89                     | 6100                               | 1.11             |
| 2              | straight      | 2.50/0.035                          | 29           | 71              | 1.70, 2.30               | 35/12                       | 90                     | 9700                               | 1.13             |
| 3              | straight      | 2.72/0.031                          | 31           | 88              | 1.50, 2.50               | 35/12                       | 78                     | 13500                              | 1.22             |
| 4              | straight      | 2.93/0.027                          | 34           | 109             | 1.30, 2.70               | 35/12                       | 88                     | 23300                              | 1.32             |
| 5              | straight      | 2.6/0.033                           | 30           | 79              | 0.80, 1.20               | 35/24                       | 97                     | 8700                               | 1.15             |
| 6 <sup>g</sup> | straight      | 2.6/0.033                           | 30           | 79              | 0.80, 1.20               | 35/24                       | 97                     | 8200                               | 1.19             |
| 7              | acute zigzag  | 3.26/0.010                          | 38           | 326             | 2.68, 8.03 <sup>h</sup>  | 35/6.0                      | 55                     | 14500                              | 1.18             |
| 8              | obtuse zigzag | 3.26/0.010                          | 38           | 326             | 2.10, 6.30 <sup>h</sup>  | 35/6.0                      | 59                     | 15400                              | 1.23             |
| 9              | pinched       | 3.26/0.010                          | 38           | 326             | 2.25, 6.75 <sup>h</sup>  | 35/6.0                      | 59                     | 16300                              | 1.24             |
| 10             | straight      | 3.26/0.010                          | 38           | 326             | 2.00, 6.00 <sup>h</sup>  | 35/6.0                      | 60                     | 18200                              | 1.31             |

<sup>a</sup> Concentration of styrene and initiator in the final mixed solution in mol/L. <sup>b</sup> Equivalents of styrene with respect to the initiator. <sup>c</sup> Pumping rates of syringes with initiator and syringe with monomer, respectively. <sup>d</sup> Reaction conditions including temperature and reaction time.

<sup>e</sup> Determined by <sup>1</sup>H NMR analysis of crude samples. <sup>f</sup> Measured by SEC using PS standards. <sup>g</sup> Polymerization was conducted continuously without washing microchannel. <sup>h</sup> Flow rates were adjusted to account for internal volumes: acute zigzag (1070 μL), obtuse zigzag (840 μL), pinched (900 μL), and straight (800 μL). These volumes correspond to measured values made on fully assembled devices.



**Fig. 4** Normalized GPC plots of polystyrenes produced within microfluidic devices. (a) Various molecular mass polymers can be produced by adjusting the relative flow rates of reagent solutions. (b) Various channel layouts are examined to determine the impact on polydispersity. Details of these polymers are listed in [Table 2](#), entries 7–10.

In [Table 2](#), entries 1–4, the reactor was cleaned, dried, and initiator was flowed through it prior to use in order to fully assure no cross-contamination between samples occurred. The flow-through design, however, allows for a variety of means of cleaning. Vigorously washing, baking, and initiator purging represent one extreme, although this can be simplified by producing several devices and exchanging them as needed. Thus, device cleaning can be carried out at a later, more convenient time. The other extreme is to simply change reagent flow rates without any cleaning or purging steps. This approach brings with it the concern that residual material from the initial sample will contaminate the following ones. Changing samples without cleaning is demonstrated in [Table 2](#), entry 6, where a reactor was switched from targeting 53 equivalents to



80 equivalents. In comparison to a reactor that had been rigorously cleaned (entry 5), there was little difference, although the PDI value was slightly higher (1.19 vs. 1.15). Samples with higher concentrations or  $M_n$ , however, may prove to be more difficult to flush. It should be noted that solvent or Argon flushing are also possible, and a cleaning regimen with appropriate rigor and convenience can be selected as needed.

Optimizing a synthesis within a batch reactor is mainly limited to reagent and reactor purification. In microreactors, however, there is added concern over the quality of mixing. Usually, flow within straight or gradually curving microfluidic channels is purely laminar, and it is assumed that reagent diffusion provides sufficient mixing. This assumption is invalid for instances when diffusion is insufficient, for example in solutions with high viscosity or high molecular weight. To address this issue, four different channel patterns were designed to explore the possibility of providing passive mixing along the length of the channel, thereby improving product quality. That is, reactions that are well mixed are expected to have relatively narrower molecular mass distributions. Finally, it is noted that patterning channels to produce passive mixing is a well documented strategy in microfluidics.<sup>9-11</sup>

In evaluating the impact of channel design, it was found that sufficient mixing is often obtained in the straight channel. For example, [Fig. 3](#) presents data obtained for relatively low molecular mass polymers synthesized within the four devices. The results suggest that the patterned channels did not consistently lower the PDI values, and in fact polymers with higher PDI values were obtained at long reaction times (*i.e.*, low total flow rates) in comparison to the straight channel. This is consistent with the simulations by Girault and coworkers, who found that zigzag channels at slow flow rates increased the effective channel width, thereby lowering the quality of mixing.<sup>46</sup> When carrying out polymerizations that have higher viscosities, however, it appears that there is a positive impact of patterning the reaction channel. These data are described in [Table 2](#), entries 7–10. Polymerizations within the devices had comparable reaction kinetics, with conversions ranging from 55% to 60% after 6 min. On the other hand, the PDI values narrowed progressively for the straight, pinched, obtuse zigzag, and acute zigzag (1.31, 1.24, 1.23, and 1.18, respectively). These results suggest that, for this particular condition, the patterned channels provide some passive mixing that improves reaction conditions, thereby narrowing the molecular mass distribution. Repeated measurements at these conditions found that the straight channel device consistently produced materials having broader PDI than the patterned channels. For these measurements, the reaction time and composition were held constant, leaving the channel design as the only major variable. However, it is noted that the total volume varied somewhat among the devices (mainly due to the variation in channel path length), and the total flow rate was adjusted to maintain a constant residence time. Ideally, however, the channel path length, total flow rate, and reaction times would be identical in all cases to facilitate comparison. Thus, further work is warranted to quantitatively determine the impact of channel design on the resulting polydispersity.

In general, channels with zigzag patterns have been demonstrated to provide two categories of passive mixing, referred to as elastic turbulence<sup>47-49</sup> and laminar recirculations.<sup>46</sup> The onset of elastic turbulence is impacted by several solution properties including the shear rate and degree of streamline curvature. With respect to living anionic polymerization, a key criterion is that the solution contains components with long relaxation times. In the work of Groisman, *et al.* and Pathak *et al.* small amounts of high molecular mass polymer,  $O$  ( $10^7$  g/mol), were added to the solutions.<sup>47,49</sup> In the case of living anionic polymerization, it is noted that polystyrene anions counterbalanced by lithium cations are known to aggregate in non-polar solvents, thereby functioning as long relaxation time additives. As an example, Fetters *et al.* found that polystyrene with styryllithium head groups assembled in benzene forming cylindrical micelles well over 100 nm in length.<sup>50</sup> Thus, attempts to create elastic turbulence, in general, should focus on solvents that induce chain aggregation, and may benefit from increases in streamline curvature (*e.g.*, channels with acute bending angles). On the other hand, mixing can also potentially be induced through laminar recirculations within zigzag channels, as was described by Girault and coworkers.<sup>46</sup> They found that the onset of laminar recirculations depended on the sample's Reynolds number, with critical values determined *via* simulation, 80, and experiment, 7. In addition, they noted that rough channel surfaces are expected to create small flow disturbances, thereby facilitating mixing at a lower Reynolds number.<sup>46</sup> Therefore, attempts to create laminar recirculation should benefit from increasing the total flow rate and by deliberately roughening the channel walls.

## Summary

This work evaluated the ability of a recently developed aluminum-Kapton microfluidic device to conduct living anionic polymerizations. Polymerizations of styrene in cyclohexane were carried out at elevated temperature (60 °C) and high monomer concentration (42%, by volume). The solution could be viewed in the device, allowing for verification that the temperature was maintained below the boiling point of cyclohexane (81 °C) at all points in the reactor. Conducting these reactions in a batch reactor results in uncontrolled heat generation with potentially dangerous rises in pressure. Moreover, the microfluidic nature of these devices allows for flexible 2D designing of the flow channel. Four flow designs were examined. In the case when moderately high molecular mass polymers with increased viscosity were made, the patterned channels appeared to lower the PDI value of the product. This result may be caused by passive mixing arising from the channel design. Further application of this work can be in systematic high throughput sample production for analysis with an integrated micro-total analysis system ( $\mu$ TAS). The rapid polymerization rates are expected to accelerate serial materials screening.

## Acknowledgements

The authors thank Dr. Steven Hudson, Dr. Thuy Chastek, and Dr. Eric Amis at NIST for their helpful suggestions and comments. T.Q.C. was supported by a NIST/National Research Council Postdoctoral Associateship. This work was carried out at the NIST Combinatorial Methods center (NCMC; [www.nist.gov/combi](http://www.nist.gov/combi)). Official contribution of NIST; not subject to copyright in the United States.

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