

ATRP IN MICROCHANNELS*

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Introduction

The range of accessible well-defined synthetic polymers expanded dramatically with the discovery of atom transfer radical polymerization (ATRP).¹ In fact, there are so many options for variations of block, statistical and gradient copolymers, not to mention graft, hyperbranched and star molecular architectures, polymer scientists have only begun to sample the tremendous range of properties and potential applications from these materials. Even basic characteristics, such as molecular weight and end-functionality, often have dramatic influence on end properties in polymers that, until recently, were not able to be prepared with narrow distributions in size.

With the adoption of combinatorial synthesis and a suite of new measurement methods practiced on very small quantities of materials, the traditional scale of materials synthesis only generates added costs in time, energy and waste. Developments in microfluidic and microreactor technologies are creating new opportunities to accelerate the pace of discovery in the area of well defined polymers. There are the simple advantages of small scale, rapid and continuous reactions in microsystems that are appealing to any problem with expensive / scarce starting materials or large numbers of products. Furthermore, there are examples of the unique benefits of high heat transfer and rapid mixing capabilities in microreactors already demonstrated in other areas of chemical synthesis.²⁻⁵

Recently, our group has begun to transfer some of these benefits to controlled radical polymerization. The microenvironment has potential applications for rapid synthesis of libraries of materials, as described here, as well as potential to enable synthesis of certain materials that remain a challenge with conventional techniques. ATRP was the first choice of reaction systems to work with due to its simplicity, versatility and the abundance of commercially available starting materials. A very logical extension can be made in these devices, however, to a range of controlled or other types of polymerizations.

Microchannel Devices. Two basic approaches are used to construct microfluidic devices and microchannels in our laboratories. Several factors must be considered when choosing materials, length scales and geometries of devices. For increased solvent resistance with a relatively inexpensive and accessible fabrication process, we used a photo-curable thiolene-based adhesive to create microchannels between two glass slides in a process described elsewhere.⁶⁻⁸ Channel dimensions are typically 250 μm to 2 mm wide and 250 μm to 1 mm deep, with configurations determined by the masks, which are prepared using simple graphics programs (Canvas)[†] and a laser printer.

To construct microchannels that may be imposed on a surface, but later removed without leaving significant residue, we mold polydimethylsiloxane (PDMS) against masters (negatives of the desired structures) prepared either from the thiolene material or SU-8[†] photoresist, depending on the desired dimensions of the channel. One of the advantages of the thiolene is its ability to cure relatively deep and/or wide structures (in some cases centimeters thick or wide) to prepare larger channels than those typically used in microfluidic applications. Channel dimensions for devices used for microchannel confined surface initiated polymerizations range from 20 μm to 1 cm in width and 500 nm to 300 μm in height.

Solution Polymerization. Recently, we reported the first ATRP inside a microfluidic device.⁹ The device used was relatively simple. Two inputs meet at a junction containing a small mixer. One solution contained monomer (2-hydroxypropyl methacrylate; HPMA) and initiator in solution, the other contained monomer and catalyst in solution. Upon contact and mixing at the junction, the polymerization was initiated. We assumed the microchannels exhibited basic plug flow on the dimensions we were sampling. Because there is currently no way to measure molecular mass and molecular mass distributions in a microchannel, we resort to conventional analysis techniques (size exclusion chromatography) which require sampling larger volumes of the output. Reaction times were based on the residence time with in the channel as the solution was immediately quenched upon exit from the device. Results showed that the polymerization was controlled in the microchannel and produced similar polymers to those prepared in traditional reactors.

More recent results,¹⁰ using a three input device have enabled rapid variations in reagent concentrations; in particular the ratio of monomer to initiator could be changed while maintaining a constant ratio of initiator to catalyst. Similar variations in any of the key variables for successful ATRP could be performed, making this device appealing for both studying the influence of reaction conditions on kinetic behavior and for preparing polymer libraries with variations of molecular properties. The first demonstration of this was the preparation of block copolymers of polyethylene oxide and HPMA.

Surface Initiated Polymerizations. We have also developed a technique to prepare arrays and gradients of surface tethered polymers on surfaces.¹¹ We use an elastomeric microchannel to confine monomer/catalyst solutions on a surface functionalized with an initiator. This enables several advances that are difficult using other methods,¹² including: (1) The surface in contact with the stamp retains initiating capacity after the stamp has been removed, as do the grafted polymers (polymerized via ATRP). (2) Utilizing multiple channels, it is possible to pattern the same surface with multiple brush configurations and layers, as flow and stoichiometry conditions can be varied from channel to channel. (3) Confined solution gradients formed inside microchannels enable fabrication of grafted libraries of statistical copolymers.

We have patterned lines of grafted polymer ranging in width from 20 μm to 1 cm. Wider samples are particularly useful for characterizing the polymer brush layers, since many instruments (ellipsometer, near edge x-ray absorption fine structure) can have footprints of several millimeters. These samples are also useful for measuring at the influence of brush layers on larger scale phenomenon such as cell adsorption and proliferation. Smaller lines are more useful for probing surface changes on a smaller scale using microscopy and for testing the influence of the brush layer properties (chemical, mechanical, etc.) and property contrast on micro- and nano-scale phenomenon such as phase separation and crystallization.

Block,¹³ gradient and statistical copolymers of functional methacrylates have been prepared using this technique in a variety of combinations.

Future Work

We are currently investigating solution ATRP in microchannels for alternate approaches to studying kinetic behavior of controlled polymerizations and as a means to prepare arrays of statistical copolymers. Integration of characterization and property measurements onto the same chips is also planned. The versatility and stability of solution gradients in the surface initiated polymerizations is also being determined. This is important for expanding the number of monomer and reaction conditions available to incorporate into grafted polymer libraries.

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[†] Certain materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that these are necessarily the best available for the purpose.

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