

Controlled Radical Polymerization in Confined Spaces

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Advanced polymeric materials in applications as diverse as tissue engineering, electronics and personal care products require superior control of a wide range of properties. From molecular properties such as molar mass and chain composition, to the properties of complex mixtures, high throughput and combinatorial techniques are providing researchers access to enormous libraries en route to both improved fundamental understanding of structure-property relationships and better products. The appeal of microreactor technology to this scientific community is three-fold: further reduction of scale in expensive specialty applications; faster, less expensive process integration in laboratory-scale investigations of complex, multi-step manufacturing protocols; and potential discovery of new and improved products from the unique microreaction environment.

The technical mission of the NIST Combinatorial Methods Center (NCCMC) has two key components: development of new library fabrication techniques and commensurate high throughput and combinatorial measurement methods. Microfluidic device fabrication methods were designed to facilitate rapid redesign and fast in-house production of the chips. Our recent work demonstrates three basic routes to using the micro-environment to prepare both gradient and discrete polymer libraries from radical polymerizations.

The first is an analog of a continuous reactor for controlled radical polymerization on a chip (CRP chip). We demonstrated the application of the CRP chip to atom transfer radical polymerization (ATRP). More recent work includes the preparation of block copolymers using the CRP chip and demonstration of a new high throughput approach to evaluation of rate behavior and, possibly, kinetic rate constants using the CRP chip. Our second route to preparing polymer libraries uses organic phase droplets in a microfluidic device to enable the synthesis of high molar mass materials and crosslinked particles, while using a lower viscosity continuous phase to drive flow through the device. The result is near monodisperse polymer particles when the composition and flow rates are held constant, and a discrete array of compositions when the contents of the droplets are varied systematically over time. The third route has a goal which is fundamentally different from the first two. Microchannel confined surface initiated polymerization (μ SIP) employs a shallow channel (between 90 nm and 300 μ m deep), formed through a patterned polydimethylsiloxane stamp, to confine a solution of monomer and catalyst over an initiator-functionalized silicon substrate. The result is a polymer grafted (brush) surface with geometry determined by the channel design and a gradient in molecular properties determined by the solution flow rate(s).