# Revolutionizing Polymer Brush Synthesis with Microfluidic Magic: Microfluidic Driven Controlled Synthesis of Finely Tailored Polymer Brushes via SI-ATRP.

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***Highlights***

- Microfluidic reactors are used for the controlled synthesis of polymer brushes.
- Outperformed conventional methods, achieving comparable or superior polymer brush characteristics.
- Controlled polymer brush structure with fewer chemicals, promising applications in many areas.

## 1. Introduction

A polymer brush (PB) is a structure that consists of densely packed ultrathin polymer chains of variable length with one end attached to a solid surface [1]. One of the polymerization techniques for PBs is the 'grafting from' method. It involves sequential polymerization of aqueous monomers onto a pre-modified surface which bears a functional group acting as an initiator. Having precise control over the thickness of the brush provides the advantage of being able to control a wide range of surface properties, including tunable hydrophobicity or hydrophilicity, modulating chemical transport, controlling cell adhesion, and tuning the properties of lubrication [2]. Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) is one of the most widely used 'grafting from' polymerization techniques [3]. The conventional synthesis of PBs via the SI-ATRP technique occurs by immersion of initiator coated surfaces into a reaction mixture of monomer and catalyst complex (on mL scale) in a tightly sealed flask attached to the Schlenk line, corresponding to a surface-area to volume ratio of more than 200 $mm^2$/mL. This conventional synthesis requires the consumption of a high concentration (on the M scale) of expensive monomers where less than 1 part in 10.000 of the monomer mixture is polymerized onto the surface. In addition to being poor in the atom economy and expensive in the consumption of chemical reagents, the conventional SI-ATRP technique does not have temporal or spatial control over the formation of PB, leading to the formation of homogeneously but randomly distributed side chains throughout the PB [4]. The application of microfluidic reactor to the synthesis of PBs via the SI-ATRP technique can overcome these drawbacks of conventional static synthesis strategies. With proper spatio-temporal control of reaction mixtures using microfluidic reactors one can increase the surface area/volume ratio by over 1000×, which not only serves to increase polymerization efficiency but also allows one to synthesize PB structures that are not possible by conventional static methods.

## 2. Methods

3D models of microfluidic reactors designed using Fusion 360 software (Fig.1a-c). Following this, 3D models were exported as .stl files. The models were then sliced for printing using PreForm software. Microfluidic reactors were printed with Formlabs High Temp resin on a Form 3+ printer. 3D printed reactors subjected to the post-processing procedure recommended by the resin manufacturer.

All solvents prior to the synthesis were degassed by freeze-pump-thaw method. To achieve the desired PB structures on the surface of gold, commercially available monomers were chosen, and different monomer flow strategies (Fig.1d-e) were applied. To compare novel flow synthesis techniques, we also conducted conventional static synthesis of PBs.

Synthesized PBs were characterized by infrared spectroscopy. Antifouling properties of PBs were investigated by surface plasmon resonance. Swelling and thickness of PBs were investigated with

ellipsometry. The surface composition of the PBs was analyzed by X-ray photoelectron spectroscopy. The wettability of the PB surface was investigated by contact angle measurements.

## 3. Results and discussion

We successfully achieved the synthesis of PBs with novel flow synthesis techniques by using 3D-printed microfluidic reactors. We studied some parameters such as flow rate, reaction times, and concentration gradients of monomer/catalyst mixtures to determine ideal microfluidic conditions for polymerization. These variations had an impact on the thickness, density, and distribution of PBs.

Comparison of our technique with conventional synthesis methods shows that we achieved PBs with similar characteristics (brush thickness, swelling, and functional capability) as those synthesized via conventional means. In some cases, the PBs synthesized in a microfluidic reactor exceeded the conventionally synthesized PBs.

The major result of applying microfluidic reactors to the synthesis of PBs was that we were able to control the structure of PBs, which is not possible with conventional synthesis techniques, while reducing the synthesis cost by using far fewer chemicals.

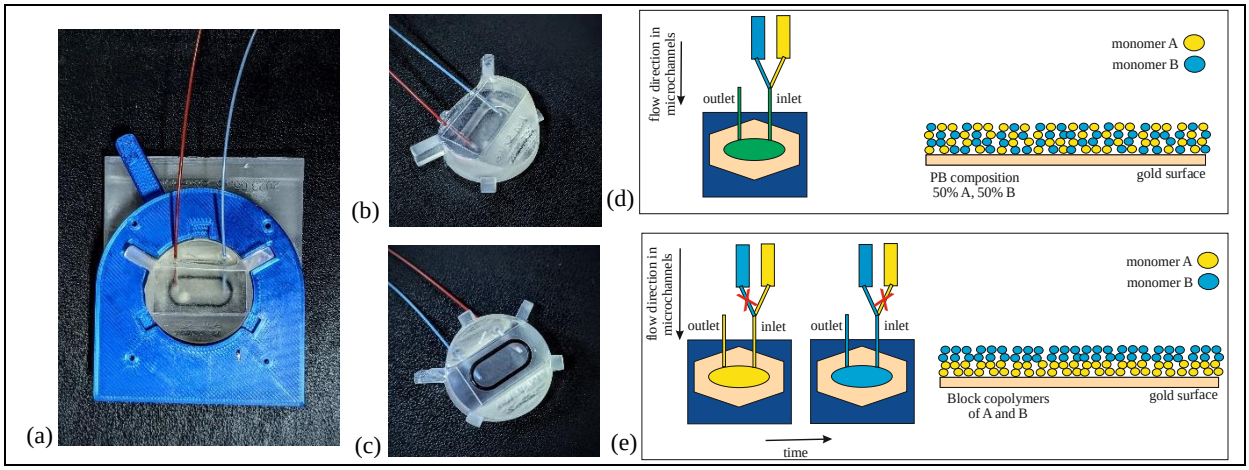


**Figure 1.** (a) 3D-printed microfluidic reactor used in the synthesis of polymer brushes. (b) Top and (c) bottom view of a 3D-printed microfluidic reactor. (d) Synthesis of PBs with distinct compositional gradients on the gold surface. By flowing a mixture of monomers through the microreactor a homogeneous mixture of monomers is obtained. (e) Synthesis of PBs with block co-polymer structure, which is formed via temporal switching of monomers.

## 4. Conclusions

We synthesized PBs on the gold surface using 3D printed microfluidic reactors that are atomically economical and capable of controlling the distinct compositional gradients of the PBs.

## References


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***Keywords***

Polymer brushes; Surface Initiated Atom Transfer Radical Polymerization; Microreactors