# Nitroxide-mediated polymerization in microfluidic devices: towards a better control of the macromolecular architecture


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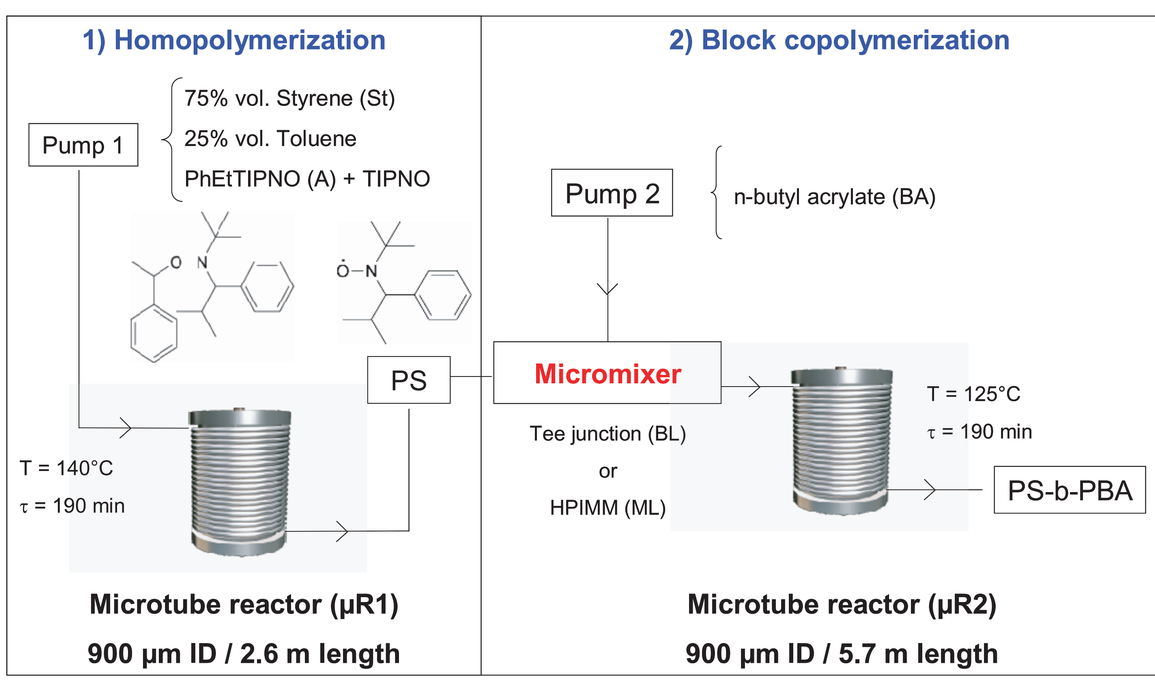
## Introduction

**Aim**: Microfluidic devices: a new tool in polymer science ?

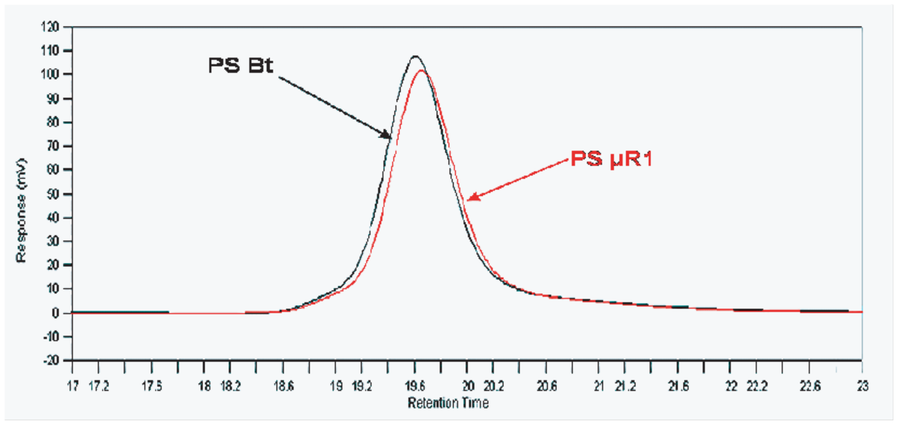
Here, we look at the styrene Nitroxide-Mediated Polymerization (NMP) with different microfluidic devices.
We are interested in its livingness by studying its copolymerization with an acrylic comonomer.
We look also at the influence of the geometry of the microfluidic devices on the control of the macromolecular architecture.

## Setup



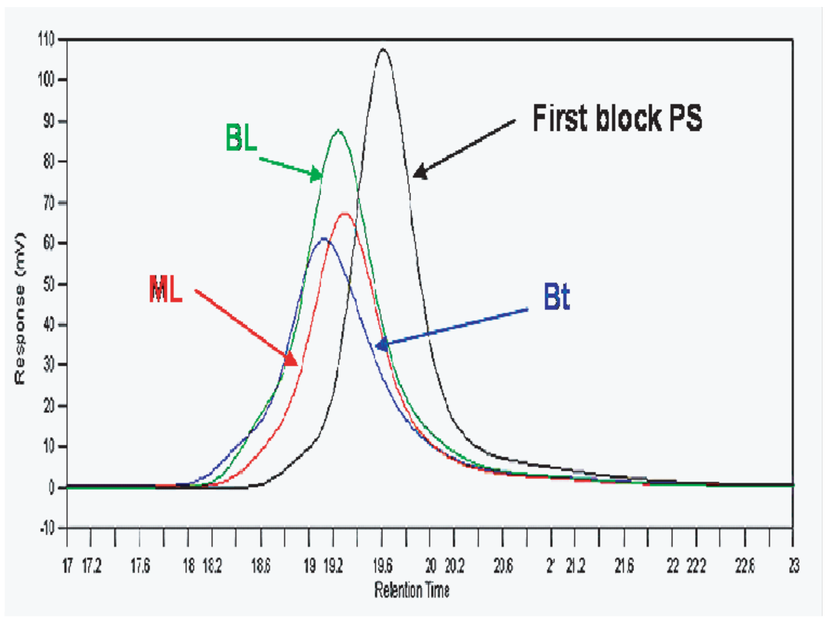

## Results

### 1) Homopolymerization



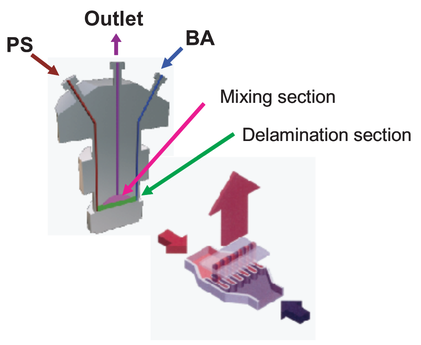

| | | |
|---|---|---|
| $M_n$ targeted (g/mol) | | 30300 |
| Conversion[b] (%) | Batch (Bt) | 65 |
| | Microreactor (μR1) | 60 |
| Theoritical $M_n$ (g/mol) | Bt | 19800 |
| | μR1 | 17500 |
| Experimental[d] $M_n$ (g/mol) | Bt | 19500 |
| | μR1 | 18300 |
| PDI[d] | Bt | 1.25 |
| | μR1 | 1.25 |

### 2) Block copolymerization

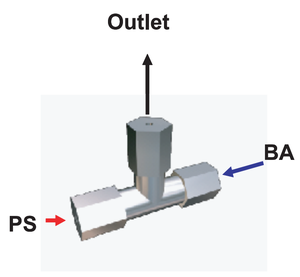



**Micromixers**

Multilamination
HPIMM (ML)

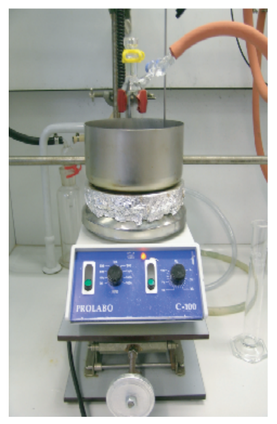



Bilamination
Tee junction (BL)




**Batch[a]**

(Bt)



| | Micromixers: Multilamination HPIMM (ML) | Micromixers: Bilamination Tee junction (BL) | Batch[a] (Bt) |
|---|---|---|---|
| Monomer conversion St/BA[c] | 90% / 14% | 87% / 4% | 80% / 39% |
| Overall conversion[b] | 33% | 25% | 43% |
| Theoritical Mn[c] (g/mol) | 30300 | 25700 | 32800 |
| Experimental Mn[d] (g/mol) | 28300 | 28200 | 29500 |
| PDI[d] | 1.22 | 1.26 | 1.32 |

[a] for comparison purpose
[b] gravimetry
[c] NMR $^1H$ measurements
[d] **without further purification of the polymers**

## Conclusion

Concerning the first block polystyrene, the results indicate that the controlled nature of the polymerization is maintained in a continuous microtube reactor.
Concerning the copolymer, the multilamination micromixer leads to the smallest PDI and allows the best control over the number-average molecular weight.

**Finally**: The use of microfluidic devices can significantly improve the control of the macromolecular architecture.
It's a new promising tool in polymer science.


Acknowledgement

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