Supporting Information

Engineering of Molecular Geometry in Bottlebrush Polymers

Dylan J. Walsh†, Sarit Dutta†, Charles E. Sing†‡*, Damien Guironnet†‡*,

†Department of Chemical and Biomolecular Engineering, University of Illinois Urbana–Champaign, Urbana, Illinois 61801, United States.
‡Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL 61801

*cesing@illinois.edu; *guironne@illinois.edu
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I. General Methods and Materials

All reactions were performed in oven dried glassware under an argon atmosphere using standard Schlenk line techniques or in an argon-filled glovebox (O₂ < 2 ppm, H₂O < 0.5 ppm) at room temperature unless otherwise specified. All solvents were dried using a solvent purification system. All commercially obtained reagents were used as received: 3-Bromopyridine (Aldrich, 99%), Ethyl Vinyl Ether (Aldrich, 99%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (Aldrich, 98%), Boric Acid (Aldrich, 99.5%), D,L-lactide (Aldrich, 99%), 1-Octanol (Aldrich, 99%).\[\text{[(H₂IMes)(3-Br-py)²(Cl)₂Ru=CHPh]}, G₃\] was synthesized according to literature and can be purchased from Aldrich.\(^1\) norOH were synthesized according to literature and norOH can be purchased from Aldrich.\(^2\) 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (Aldrich, 98%) and δ-Valerolactone (Aldrich, \() was distilled from CaH₂ prior to use. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (Aldrich, 98%) was sublimed prior to use.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE III 500 MHz. Spectra are reported in ppm and referenced to the residual solvent signal: CDCl₃ (\(^1\)H 7.26 ppm, \(^13\)C 77.16 ppm), C₆H₆ (\(^1\)H 7.16 ppm, \(^13\)C 128 ppm), CD₂Cl₂ (\(^1\)H 5.32 ppm).

Gel Permeation Chromatography (GPC) was performed using a Tosoh Ecosec HLC-8320GPC at 40 °C fitted with a reference column (6.0 mm ID x 15 cm), a guard column (6.0 mm ID x 4.0 cm x 5 μm), and two analytical columns (7.8 mm ID x 30 cm x 5 μm). The reference flow rate is 0.5 mL min⁻¹ while the analytical column is at 1.0 mL·min⁻¹. THF (HPLC grade) was used as the eluent, and polystyrene standards (15 points ranging from 500 Mw to 8.42 million Mw) were used as the general calibration. An additional calibration was created specifically for linear polylactic acid and only used for linear polylactic acid (10 points ranging from 500 Mw to 10,000 Mw).

Triple Detection Gel Permeation Chromatography (GPC) was performed using a Viscotek GPCmax pump and TDA302 triple detector (Refractive Index, 90° and 7° light scattering, Viscometer) at 35 °C fitted with two mixed-bed analytical columns (PolyAnalytik PAS-M: 8 mmID x 30 cm length, 10 μm particles, exclusion limit 20,000,000 Da relative to polystyrene). The flowrate was 1.0 mL‘min⁻¹. THF (HPLC grade) was used as the eluent. The detectors were calibrated with a narrow polystyrene standard (Mₘ= 99,000 Da). Polymer solutions were prepared at a known concentration (ca. 5 mg/mL) and an injection volume of 30 μL was used. dn/dc values for the bottlebrush polymers were obtained for each injection by assuming 100% mass elution from the columns. (Performed by PolyAnalytik Inc.)

Abbreviations/Definitions:

GPC: Refractive index Gel permeation chromatography with respect to polystyrene standards

\(t\)-GPC: Triple Detection Gel Permeation Chromatography

NMR: Nuclear Magnetic Resonance

AFM: Atomic force microscopy

cBB: cylindrical bottlebrush

hBB: hourglass bottlebrush

fBB: football bottlebrush

bowBB: bowtie bottlebrush

norOH: 5-Norbornene-2-methanol, or (bicyclo[2.2.1]hept-5-en-2-yl)methanol

G₃: 3\(^{\text{rd}}\) generation Grubbs catalyst (3-bromo pyridine version)
**DBU:** 1,8-Diazabicyclo[5.4.0]undec-7-ene
**TBD:** 1,5,7-Triazabicyclo[4.4.0]dec-5-ene
**LA:** Lactide
**VL:** δ-Valerolactone
**PLA:** Poly(lactic acid)
**PVL:** Poly(δ-Valerolactone)
**N:** Degree of polymerization

**LA Buildup:** The lactide that has been unconverted in the ROMP pot (second vessel). Calculated from $^1$H NMR of aliquots from the ROMP pot

$$LA_{\text{Buildup}} = \left( \frac{\text{Mole of LA fed in the ROMP pot}}{\text{unreacted LA}} \right) \frac{\text{unreacted LA}}{\text{unreacted LA} + \text{PLA}}$$  

**VL Buildup:** The valerolactone that has been unconverted in the ROMP pot (second vessel). Calculated from $^1$H NMR of aliquots from the ROMP pot

$$VL_{\text{Buildup}} = \left( \frac{\text{Mole of VL feed in the ROMP pot}}{\text{unreacted VL}} \right) \frac{\text{unreacted VL}}{\text{unreacted VL} + \text{PVL}}$$
Unreacted macromonomer: The unreacted macromonomer in the ROMP pot with respect to all the norbornene in the entire system initially.

\[
Unreacted \text{ macromonomer}(NMR) = 1 - \frac{\text{mmol Nor ROMP}}{\text{mmol Nor system initially}} \quad \text{S3}
\]

Calculated from \textsuperscript{1}H NMR of aliquots from the ROMP pot.
Also, calculated from GPC of aliquots from the ROMP pot.

\[
Unreacted \text{ macromonomer}(GPC) = 1 - \frac{\text{Area of macromonomer}}{\text{Area of (macromonomer + bottlebrush)}}
\]
II. Reactor Setup

The reactor consists of two syringes, tubing and a 20 ml vial. Glass syringes were used since plastic syringes can’t handle the mild pressure that builds up in the system and it was found that the plasticizers leach out of PP syringes killing G3. The tubing is PEEK tubing; stainless steel was used initially, but it was found that DBU partially reacts with the steel. A positive pressure of argon is maintained by a needle through the septum of the vial.

Figure S1: Scheme of the reactor setup correlated back to the real-world reactor setup

Specialty Parts (for one setup):

2 x syringe pumps connect to a computer (kd Scientific, Legato® 101)
1 x 10 ml glass syringe (Hamilton, Model Number: 1010, PTFE Luer Lock)
1 x 2.5 ml glass syringe (Hamilton, Model Number: 1002, PTFE Luer Lock)
2 x syringe to PEEK connector (Hamilton, Model Number: 55751-01 and 55752-01 and 55753-01)
1 x Tee Assembly High Pressure PEEK .020 thru hole (IDEX Health & Science, Part #: P-715)
25 ft. of PEEK Tubing 1/16” OD 0.020” ID (IDEX Health & Science, Part #: 1532L)
20 mL vials with TFE septa (Chemglass, Item #: CG-4904-01)
III. Ring Opening Polymerization of Lactide (Batch)

We explored the kinetics of the ROP of lactide since the rate law and rate constant are inputs for the mathematical model. Our approach of synthesizing architecture-controlled bottlebrush polymers involves, holding the initial concentration of LA and initiator (norOH) constant while changing the flow rate of DBU. Thus, a wide range of DBU loading were examined with batch reactions.

A represented procedure for ROP of lactide with DBU (adapted from literature)

![Reaction mechanism](image)

To an oven-dried 20 mL glass vial, lactide (1.0g, 6.94 mmol, 0.6 ml*) and 1-octanol (12.84 mg, 0.099 mmol) dissolved in 5.9 mL of THF. The polymerization was initiated by adding DBU (30 mg, 0.197 mmol) dissolved in 1 mL of THF. At various time point (1, 3, 8, 12, 23, 39 min) 70 μL aliquots were removed from the reaction mixture and were injected into vials containing a large excess of acetic acid to be analyzed by GPC.

Notes:
*The effective volume of dissolved monomer in a 0.92 M THF solution (0.0865 ml of THF/mmol of lactide).

Table S1: Data for ROP of lactide with various amounts of DBU

<table>
<thead>
<tr>
<th>[DBU] (mM)</th>
<th>Time (min)</th>
<th>Mn (g/mol)</th>
<th>Mn/Mn0</th>
<th>Conv.</th>
<th>[LA] (M)</th>
<th>rate (M/min)</th>
<th>[LA] avg. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.2</td>
<td>1</td>
<td>900</td>
<td>1.17</td>
<td>8.9%</td>
<td>0.838</td>
<td>0.082</td>
<td>0.879</td>
</tr>
<tr>
<td>3</td>
<td>2430</td>
<td>1.08</td>
<td>24.1%</td>
<td>0.698</td>
<td>0.070</td>
<td>0.768</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4770</td>
<td>1.06</td>
<td>47.2%</td>
<td>0.485</td>
<td>0.043</td>
<td>0.592</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5800</td>
<td>1.05</td>
<td>57.4%</td>
<td>0.392</td>
<td>0.023</td>
<td>0.439</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>7310</td>
<td>1.08</td>
<td>72.3%</td>
<td>0.255</td>
<td>0.012</td>
<td>0.323</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>8260</td>
<td>1.10</td>
<td>81.7%</td>
<td>0.168</td>
<td>0.005</td>
<td>0.211</td>
<td></td>
</tr>
<tr>
<td>15.7</td>
<td>2</td>
<td>1110</td>
<td>1.13</td>
<td>10.9%</td>
<td>0.819</td>
<td>0.050</td>
<td>0.870</td>
</tr>
<tr>
<td>8</td>
<td>3550</td>
<td>1.06</td>
<td>35.2%</td>
<td>0.596</td>
<td>0.037</td>
<td>0.708</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>5000</td>
<td>1.06</td>
<td>49.5%</td>
<td>0.464</td>
<td>0.022</td>
<td>0.530</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>6500</td>
<td>1.05</td>
<td>64.4%</td>
<td>0.328</td>
<td>0.012</td>
<td>0.396</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>7550</td>
<td>1.06</td>
<td>74.7%</td>
<td>0.233</td>
<td>0.007</td>
<td>0.280</td>
<td></td>
</tr>
<tr>
<td>59.33</td>
<td>8280</td>
<td>1.10</td>
<td>81.9%</td>
<td>0.166</td>
<td>0.003</td>
<td>0.199</td>
<td></td>
</tr>
<tr>
<td>10.5</td>
<td>5</td>
<td>1820</td>
<td>1.10</td>
<td>18.0%</td>
<td>0.754</td>
<td>0.033</td>
<td>0.837</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>4250</td>
<td>1.05</td>
<td>42.1%</td>
<td>0.533</td>
<td>0.022</td>
<td>0.644</td>
</tr>
<tr>
<td>Time (min)</td>
<td>Mn (g/mol)</td>
<td>Mw/Mn</td>
<td>Conversion (%)</td>
<td>Mw (g/mol)</td>
<td>Mn (g/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>-------</td>
<td>---------------</td>
<td>------------</td>
<td>------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10,000</td>
<td>1.05</td>
<td>11.7%</td>
<td>0.413</td>
<td>0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5560</td>
<td>1.08</td>
<td>22.4%</td>
<td>0.714</td>
<td>0.021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3770</td>
<td>1.06</td>
<td>37.3%</td>
<td>0.577</td>
<td>0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5630</td>
<td>1.05</td>
<td>55.7%</td>
<td>0.407</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>6680</td>
<td>1.06</td>
<td>66.2%</td>
<td>0.311</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>94</td>
<td>7750</td>
<td>1.07</td>
<td>76.7%</td>
<td>0.214</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>8460</td>
<td>1.09</td>
<td>83.7%</td>
<td>0.150</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: [OH] = 0.0131 M, [LA] = 0.92 M, THF, 25 °C; Mn and Mw/Mn are calculated from GPC with respect to PLA standards. Conversion = Mn(GPC)/Mn(theory)

LA_{avg} = \frac{[LA]_{t_{i-1}} + [LA]_{t_i}}{2}

Figure S2: M_n vs time for the ROP of lactide with various amounts of DBU
We tried plotting the data from Table S1 onto a ln([LA]/[LA]₀) plot (this assumes that LA is first order in the rate law) and non-linear lines were observed. This suggests that the LA is not first order in the rate law.

Thus, an alternative analysis was performed. A general rate law was proposed, and an approximation for the derivative was made.

\[
\frac{d[LA]}{dt} = -k_{app}[OH]^a[DBU]^b[LA]^c
\]

\[
\frac{d[LA]}{dt} \approx \frac{[LA]_{t_i} - [LA]_{t_{i-1}}}{t_i - t_{i-1}} = -k_{app}[OH]^a[DBU]^b[LA]_{avg}^c
\]

\[
[LA]_{avg} = \frac{[LA]_{t_{i-1}} + [LA]_{t_i}}{2}
\]

\[
\ln\left(\frac{[LA]_{t_{i-1}} - [LA]_{t_i}}{t_i - t_{i-1}}\right) = \ln(k_{app}[OH]^a[DBU]^b[LA]_{avg}^c)
\]

\[
\ln(\text{rate}) = \ln\left(\frac{[LA]_{t_{i-1}} - [LA]_{t_i}}{t_i - t_{i-1}}\right) = c \ln([LA]_{avg}) + \ln(k_{app}[OH]^a[DBU]^b)
\]

(a, b, x are unknown constants)

\[
y = mx + b
\]

Figure S3: Rate vs lactide concentration for the ROP of lactide with various amounts of DBU

The conclusions from Figure S3 is that LA order varies from 1.78 to 3.2. We will choose a LA order of 1.8 for our mathematical derivation since it approximates our area of interest the best.
The conclusions from Figure S4 is that DBU is first order over our area of interest.

Next we wanted to check that the initiator (OH) is first order for our concentration of interest. Note that the concentration of OH remains constant in our flow system so only a small range of OH concentration is examined.

Table S2: Data for the ROP of lactide with various amounts of initiator (OH)

<table>
<thead>
<tr>
<th>[OH] (M)</th>
<th>Time (min)</th>
<th>$M_n$(g/mol)</th>
<th>$M_w/M_n$</th>
<th>Conv.</th>
<th>[LA] (M)</th>
<th>rate (M/min)</th>
<th>[LA] avg. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0262</td>
<td>2</td>
<td>970</td>
<td>1.13</td>
<td>19.2%</td>
<td>0.744</td>
<td>0.088</td>
<td>0.832</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2390</td>
<td>1.10</td>
<td>47.3%</td>
<td>0.485</td>
<td>0.043</td>
<td>0.702</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>2950</td>
<td>1.08</td>
<td>58.3%</td>
<td>0.383</td>
<td>0.025</td>
<td>0.652</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3670</td>
<td>1.08</td>
<td>72.6%</td>
<td>0.252</td>
<td>0.016</td>
<td>0.586</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4120</td>
<td>1.08</td>
<td>81.6%</td>
<td>0.169</td>
<td>0.008</td>
<td>0.545</td>
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<td></td>
<td>60</td>
<td>4700</td>
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<td>93.1%</td>
<td>0.063</td>
<td>0.004</td>
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</tr>
<tr>
<td>0.0131</td>
<td>5</td>
<td>2010</td>
<td>1.09</td>
<td>19.9%</td>
<td>0.737</td>
<td>0.037</td>
<td>0.829</td>
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<td>15</td>
<td>4450</td>
<td>1.05</td>
<td>44.1%</td>
<td>0.514</td>
<td>0.022</td>
<td>0.717</td>
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<td></td>
<td>25</td>
<td>5850</td>
<td>1.05</td>
<td>57.9%</td>
<td>0.387</td>
<td>0.013</td>
<td>0.654</td>
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<tr>
<td></td>
<td>40</td>
<td>7110</td>
<td>1.06</td>
<td>70.3%</td>
<td>0.273</td>
<td>0.008</td>
<td>0.596</td>
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<td></td>
<td>59</td>
<td>7960</td>
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<td>78.8%</td>
<td>0.195</td>
<td>0.004</td>
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<tr>
<td></td>
<td>120</td>
<td>8970</td>
<td>1.15</td>
<td>88.8%</td>
<td>0.103</td>
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</tr>
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<td>0.00655</td>
<td>10</td>
<td>3830</td>
<td>1.06</td>
<td>18.9%</td>
<td>0.746</td>
<td>0.017</td>
<td>0.833</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8480</td>
<td>1.04</td>
<td>42.0%</td>
<td>0.534</td>
<td>0.011</td>
<td>0.727</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>10,900</td>
<td>1.05</td>
<td>53.9%</td>
<td>0.424</td>
<td>0.005</td>
<td>0.672</td>
</tr>
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<td></td>
<td>80</td>
<td>13,100</td>
<td>1.08</td>
<td>64.7%</td>
<td>0.325</td>
<td>0.003</td>
<td>0.622</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>14,700</td>
<td>1.11</td>
<td>72.7%</td>
<td>0.251</td>
<td>0.002</td>
<td>0.585</td>
</tr>
</tbody>
</table>

*aReaction conditions: [DBU]= 0.0105 M, [LA]=0.92 M, THF, 25 °C; $M_n$ and $M_w/M_n$ are calculated from GPC with respect to PLA standards.
Figure S5: $M_n$ vs time for the ROP of lactide with various amounts of OH

Figure S6: Rate vs lactide concentration for the ROP of lactide with various amounts of OH
The conclusion of **Figure S7** is that the ROP of OH if first order in our narrow experimental range.

Thus our proposed rate law is as follows:

\[
\frac{d[LA]}{dt} = -k_{app}[OH]^1[DBU]^1[LA]^{1.8} \tag{S8}
\]

Integrating the rate law gives the following equation:

\[
\frac{1}{[LA]_0^{0.8}} - \frac{1}{[LA]^{0.8}} = -\frac{k_{app}[DBU][OH]t}{1.25} \tag{S9}
\]

We can now obtain the \( k_{app} \) by re-plotting the data from **Table S1** according to the previous equation.
Figure S8: Plot of data from Table S1 with respect to the new rate law

The slope of Figure S8 is defined by:

\[
Slope_{(\text{Figure S8})} = \frac{k_{\text{app}} [\text{DBU}] [\text{OH}]}{1.25}
\]

Figure S9: Plot of the slopes from Figure S8 vs [DBU]

When the slopes are plotted against [DBU], a second plot can be formed where that new slope means:

\[
Slope_{(\text{Figure S9})} = \frac{k_{\text{app}} [\text{OH}]}{1.25} = 3.046
\]
Which allows us to obtain the rate constant.

\[ k_{app} = 290 \frac{1}{M^{1.8} \text{min}} \]

The following is the rate law for ROP lactide that we will use within the following limits:

\[
0 \leq [DBU] \leq 0.0262 \text{ } M \\
0.00655 \text{ } M \leq [OH] \leq 0.0262 \text{ } M \\
0 \leq [LA] \leq 0.92 \text{ } M
\]

THF at 25 °C

\[
\frac{d[LA]}{dt} = -290 \frac{1}{M^{1.8} \text{min}} [OH]^1[DBU]^1[LA]^{1.8} \\
\frac{1}{[LA]_o^{0.8}} - \frac{1}{[LA]^{0.8}} = -232 \frac{1}{M^{1.8} \text{min}} [DBU][OH]t
\]

**IV. Derivation of Flow Rate Equation**

The goal of this methodology is to be able to draw any bottlebrush contour/profile and then synthesize it. To achieve this goal we developed a flow system with two syringes, a long length of tubing, and a collection pot. One syringe has the brush monomer and initiator, and the second syringe has brush catalyst. The collection pot contains the backbone catalyst and quenching agent.

**Syringe 2:**
\( Q_{syn2}, [\text{Cat}_{syn1}] \)

**Syringe 1:**
\( Q_{syn1}, [I_{syn1}], [M_{syn1}] \)

**Collection Pot**
\( n_{bb,cat} \)

*Figure S10: Labeled schematic of the flow system*
With this configuration, the ratio of brush monomer to initiator is fixed (i.e. max brush length is fixed). Thus to control the length of the brushes, the conversion of brush monomer will need to be control in the tubing. The conversion of the brush monomer can be controlled by holding the flow rate of syringe 1 constant and changing the flow rate of syringe 2. This changes the concentration of catalyst in each plug, thus the rate of polymerization will be different in each plug resulting in different brush lengths in each plug.

This approach requires the derivation of an equation to convert a bottlebrush contour/profile to the syringe pump flow rates. This will be broken into 3 steps:

1. Backbone length to time conversion
2. Flow design equation
3. Combining the derivations

**Glossary of symbols:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>Time</td>
<td>min</td>
</tr>
<tr>
<td>$N_{bb}$</td>
<td>Degree of polymerization backbone</td>
<td>DL</td>
</tr>
<tr>
<td>$N_{brush}$</td>
<td>Degree of polymerization brush</td>
<td>DL</td>
</tr>
<tr>
<td>$N_{syn \ max brush}$</td>
<td>Degree of polymerization brush at complete monomer conversion</td>
<td>DL</td>
</tr>
<tr>
<td>$Q_{syn1}$</td>
<td>Volumetric flow rate of syringe 1 (monomer and initiator)</td>
<td>ml/min</td>
</tr>
<tr>
<td>$Q_{syn2}$</td>
<td>Volumetric flow rate of syringe 2 (brush catalyst)</td>
<td>ml/min</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow rate in tubular reactor ($Q = Q_{syn1} + Q_{syn2}$)</td>
<td>ml/min</td>
</tr>
<tr>
<td>$[I_{syn1}]$</td>
<td>Concentration of initiator in syringe 1</td>
<td>M</td>
</tr>
<tr>
<td>$[M_{syn1}]$</td>
<td>Concentration of brush monomer in syringe 1</td>
<td>M</td>
</tr>
<tr>
<td>$[Cat_{syn2}]$</td>
<td>Concentration of brush catalyst in syringe 2</td>
<td>M</td>
</tr>
<tr>
<td>$[I]$</td>
<td>Concentration of initiator in tubular reactor</td>
<td>M</td>
</tr>
<tr>
<td>$[M]$</td>
<td>Concentration of brush monomer in tubular reactor</td>
<td>M</td>
</tr>
<tr>
<td>$[Cat]$</td>
<td>Concentration of brush catalyst in tubular reactor</td>
<td>M</td>
</tr>
<tr>
<td>$n_{bb,cat}$</td>
<td>Moles of backbone catalyst</td>
<td>mol</td>
</tr>
<tr>
<td>$x_{M}$</td>
<td>Conversion of brush monomer</td>
<td>DL</td>
</tr>
<tr>
<td>$F_i$</td>
<td>Molar flow rate of species 'i'</td>
<td>mol/min</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
<td>ml</td>
</tr>
<tr>
<td>$r_{brush}$</td>
<td>Rate of reaction, brush polymerization</td>
<td>mol/(min ml)</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant for brush polymerization</td>
<td>variable</td>
</tr>
</tbody>
</table>

**1. Backbone length to time conversion**

The flow rate of syringe 1 is a fixed value set such that the molar flow rate of initiator entering the collection pot will be sufficiently slow enough to maintain a very low concentration of macronomomers (i.e. no buildup of macronomer). This means that the degree of polymerization of the backbone ($N_{bb}$) is related to the time ($t$).
Definition of $N_{bb}$:

$$N_{bb} = \frac{\text{moles of I out of syr. 1}}{\text{moles bb cat}} = \int_0^t Q_{syn1}[I_{syn1}]dt$$

Integration ($Q_{syn1}$, $[Nor_{syn1}]$ are constants)

$$N_{bb} = \frac{[I_{syn1}]Q_{syn1}t}{n_{bb,cat}}$$

2. Flow design equation

The second step of the derivation requires converting the length of the brushes ($N_{brush}$) back to brush catalyst concentration. This can be done by relating the brush length to the conversion of brush monomer ($x_M$), then relating conversion back to the rate law which contains the brush catalyst concentration, i.e. flow design equation.

The derivation begins with relating brush length to conversion.

$$N_{brush} = N_{brush}^{syn max} x_M$$

To determine the conversion of monomer in a flow reactor, the control volume must be defined. In the case of a cylindrical pipe a cylinder will be considered.

From the control volume, we can write a mole balance around it. This provide a way to account for change in brush monomer within an infinitely thin control volume, which can be used to integrate over the total length of the reactor resulting in an equation that relates conversion to known system properties.

$$\text{In} - \text{Out} + \text{Generation} - \text{Consumption} = \text{Accumulation}$$

‘In’ = molar flow rate of monomer into the control volume = $F_M$

‘Out’ = molar flow rate of monomer out the control volume, which is equal to what goes in plus some differential change due to reaction. = $F_M + dF_M$

‘Generation’ = No reaction is producing monomer; thus this is zero = 0

‘Consumption’= rate of monomer consumption within the control volume = $r_{brush}dV$

‘Accumulation’ = rate of monomer accumulating in the control volume. The molar monomer flow rate is held constant in the experiments in this manuscript, thus there is no accumulation = 0
\[ F_M - (F_M + dF_M) + r_{\text{brush}} dV = 0 \] 

S17

Rearranging.

\[ \frac{dF_M}{dV} = -r_{\text{brush}} \] 

S18

Plugging an arbitrary rate law.

\[ -r_{\text{brush}} = \frac{d[M]}{dt} = -k[I]^a[\text{Cat}]^b[M]^c \] 

S19

For the current derivation below \( c \neq 1 \). (the solution for \( c=1 \) will be provided at the end of the section) 

The next step is to plug the rate law, equation S19, into the differential equation, equation S18.

\[ \frac{dF_M}{dV} = -k[I]^a[\text{Cat}]^b[M]^c \] 

S20

The concentration now will be converted into molar flowrates, \([i] = \frac{F_i}{Q}\).

\[ \frac{dF_M}{dV} = -\frac{kF_i^aF_{\text{cat}}^bF_M^c}{Q^{a+b+c}} \] 

S21

The volume derivative can be transformed into a derivative with respect to the axial length, \( V = \pi R^2 z \).

\[ \frac{dF_M}{dz} = -\frac{\pi R^2 kF_i^aF_{\text{cat}}^bF_M^c}{Q^{a+b+c}} \] 

S22

The general differential equation S22 can be solved with the initial condition \( F_M = F_{M,o} @ z = 0 \). This initial condition states that the molar flow rate of the brush monomer is known at the start of the tubular reactor. This can be calculated with \( F_{M,o} = Q_{\text{syn}1}[M_{\text{syn}1}] \). Thus the integration is as follows. \{Prime notation is added to \( F_M \) to differentiate the function \( F_M^c \) from the bounds \( (F_M, F_{M,o}) \}.

\[ \int_{F_{M,o}}^{F_M} \frac{dF_M'}{F_M^c} = -\frac{(\pi R^2)kF_i^aF_{\text{cat}}^b}{Q^{a+b+c}} \int_0^z dz \]

S23

\[ \left( -\frac{F_M^{1-c}}{c-1} - \left( \frac{F_{M,o}^{1-c}}{c-1} \right) \right) = \frac{F_{M,o}^{1-c}}{c-1} - \frac{F_M^{1-c}}{c-1} = -\left( \frac{\pi R^2)kF_i^aF_{\text{cat}}^b}{Q^{a+b+c}} \right) \frac{z}{c-1} \]

S24

The next step in the derivation is to replace the brush monomer molar flow rate with conversion, \( F_M = (1 - x_M)F_{M,o} \).

\[ \frac{F_{M,o}^{1-c}}{c-1} - \frac{(1 - x_M)F_{M,o}^{1-c}}{c-1} = -\left( \frac{\pi R^2)kF_i^aF_{\text{cat}}^b}{Q^{a+b+c}} \right) \frac{z}{c-1} \]

S25

### 3. Combining the derivations

So far, the architecture of the bottlebrush has not entered into the derivation. To do so, an arbitrary profile equation will be represented with a general function notation, equation S26.

\[ N_{\text{brush}} = f(N_{bb}) \] 

S26

The profile function can now be transformed into the time domain with equation S15.

\[ N_{\text{brush}} = f\left( \frac{L_{\text{syn}1}Q_{\text{syn}1}t}{n_{bb,\text{cat}}} \right) \] 

S27

Next, the brush length can be replaced with conversion from equation S16.
With the definition of conversion, we can now plug it into equation S25.

\[
x_M = \frac{1}{N_{\text{brush}}^{\text{syn max}}} f \left( \frac{[I_{\text{syn1}}]Q_{\text{syn1}}t}{n_{\text{bb,cat}}} \right)
\]

\[S28\]

The goal of this derivation was to get \( Q_{\text{syn2}} \) vs. \( t \). \( Q_{\text{syn2}} \) is present in equation S29 in the molar flow rate of catalyst, \( F_{\text{cat}} = [\text{cat}_{\text{syn2}}]Q_{\text{syn2}} \), and in the flow rate of the tubular reactor, \( Q = Q_{\text{syn1}} + Q_{\text{syn2}} \). The following will attempt to isolate \( Q_{\text{syn2}} \) to the left side and time on the right and will evaluate the equation where \( z=L \).

\[
\frac{F_{1-c}^{1-c}}{c-1} = \frac{1}{N_{\text{brush}}^{\text{syn max}}} f \left( \frac{[I_{\text{syn1}}]Q_{\text{syn1}}t}{n_{\text{bb,cat}}} \right) F_{M,0} \left( 1 - \frac{1}{(\pi R^2)kF_I^aF_{\text{cat}}^b} \right)^{1-c} = - \frac{(\pi R^2)kF_I^a [\text{cat}_{\text{syn2}}]^b Q_{\text{syn2}}}{Q_{\text{syn1}} + Q_{\text{syn2}}} z^{1-c}
\]

\[S29\]

Equation S31 provides a general solution to any rate law taking the form of equation S20. In the case were \( c=1 \), the same derivation can be performed to get equation S32.

\[
\frac{Q_{\text{syn2}}^b}{(Q_{\text{syn1}} + Q_{\text{syn2}})^a+1} = - \frac{1}{(\pi R^2)kF_I^a [\text{cat}_{\text{syn2}}]^b} \ln \left( 1 - \frac{f \left( \frac{[I_{\text{syn1}}]Q_{\text{syn1}}t}{n_{\text{bb,cat}}} \right)}{N_{\text{brush}}^{\text{syn max}}} \right)
\]

\[S30\]

\[
\frac{Q_{\text{syn2}}^b}{(Q_{\text{syn1}} + Q_{\text{syn2}})^a+1} = - \frac{1}{(\pi R^2)kF_I^a [\text{cat}_{\text{syn2}}]^b} \ln \left( 1 - \frac{f \left( \frac{[I_{\text{syn1}}]Q_{\text{syn1}}t}{n_{\text{bb,cat}}} \right)}{N_{\text{brush}}^{\text{syn max}}} \right)
\]

\[S32\]

For the ring opening polymerization of lactide using a DBU catalyst we equation 32 as the general equation we will use for all the experiments in this manuscript.

\[
\frac{Q_{\text{syn2}}^b}{(Q_{\text{syn1}} + Q_{\text{syn2}})^a+1} = - \frac{1}{(\pi R^2)kF_I^a [\text{cat}_{\text{syn2}}]^b} \ln \left( 1 - \frac{f \left( \frac{[\text{NorO}_{\text{syn1}}]Q_{\text{syn1}}t}{n_{\text{cat}}} \right)}{N_{\text{brush}}^{\text{syn max}}} \right)^{-0.8}
\]

\[S33\]

V. Ring Opening Polymerization of Lactide (Flow)

With detailed ROP of lactide kinetics and a fully derived flow rate equation (equation S33), this section will implement this for the ROP of lactide in flow. We will run flow experiments with the same DBU flow rates that we anticipate using in the bottlebrush synthesis. Samples will be collected periodically at the exit of the flow system and analyzed by GPC or NMR. These aliquots will then be plotted against the theoretical profiles. A match between theory and experiments will validate that our mathematical model and provide direct evidence of the architecture of the bottlebrush that will be produced in future experiments.
The experimental setup for the ROP of lactide flow
(this setup was used for the three experiments below; football, hourglass, bowtie)

In a glovebox, two solutions were generated in oven-dried glass vials:

1. Lactide (1.5g, 10.4 mmol, 0.9 mL*), octanol (19.4 mg, 0.149 mmol), 10.4 mL of THF
2. DBU (50 mg, 0.328 mmol, 0.063 ml), 1.03 mL THF

To setup up the flow system, a 10 mL glass syringe was filled with the lactide solution, and a 2.5 mL glass syringe was filled with the DBU solution. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps. Once the syringes were set up, the syringe pumps were activated through the computer. Once liquid began exiting the tube, samples were taken by collecting 2 drops (~15 μL) of the reaction mixture in a vial of 0.1 M acetic acid in THF or CDCl$_3$. The samples were then analyzed by GPC and/or NMR.

Notes:
*The effective volume of dissolved monomer in a 0.9 M THF solution (0.0865 ml of THF/mmol of lactide).

The flow ROP of lactide with a football profile

The following is the input need for the MATLAB code.
The following plot was generated from the MATLAB code solving equation S33 given the inputs above.

**Figure S12:** DBU flowrate for the football ROP of lactide
Figure S13: Predicted (orange line) and experimental (blue dots) data for the football ROP of lactide.

Figure S14: GPC chromatograms for the football ROP of lactide.
The flow ROP of lactide with an hourglass profile

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>hourglass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile Function</td>
<td>$N_{brush} = 0.007N_{bb}^2 - 1.4N_{bb} + 85$</td>
</tr>
<tr>
<td>$F_{Nor} = \left[N_{or_{syn1}}\right]Q_{syn1}$</td>
<td>(0.0131 M) 0.125 ml/min = 0.00164 mmol/min</td>
</tr>
<tr>
<td>$F_{L_{A_o}} = \left[L_{A_{syn1}}\right]Q_{syn1}$</td>
<td>(0.92 M) 0.125 ml/min = 0.115 mmol/min</td>
</tr>
<tr>
<td>$[DBU_{syn2}]$</td>
<td>0.3 M</td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>0.000493 mmol</td>
</tr>
<tr>
<td>$N_{syn max _brush} = 2 \cdot \frac{[L_{A_{syn1}}]}{[N_{or_{syn1}}]}$</td>
<td>$2 \cdot \frac{0.92 M}{0.0131 M} = 140$</td>
</tr>
<tr>
<td>$Q_{syn1}$</td>
<td>0.125 ml/min</td>
</tr>
<tr>
<td>$R$</td>
<td>0.0254 cm</td>
</tr>
<tr>
<td>$L$</td>
<td>762 cm</td>
</tr>
<tr>
<td>$k_{rop}$</td>
<td>$290 \cdot \frac{1}{M^{1.8} \cdot \text{min}}$</td>
</tr>
</tbody>
</table>

The following plot was generated from the MATLAB code solving equation S33 given the inputs above.

Figure S15: DBU flowrate for the hourglass ROP of lactide.
Figure S16: Predicted (orange line) and experimental (blue dots) data for the hourglass ROP of lactide.

Figure S17: GPC chromatograms for the hourglass ROP of lactide.
The flow ROP of lactide with a bowtie profile

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>bowtie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile Function</td>
<td>$N_{brush} = \begin{cases} 75 - N_{bb} &amp; 0 &lt; N_{bb} &lt; 75 \ 75 &amp; 75 &lt; N_{bb} &lt; 125 \ N_{bb} - 125 &amp; 125 &lt; N_{bb} &lt; 200 \end{cases}$</td>
</tr>
<tr>
<td>$F_{Nor} = [N_{or_{syn1}}]Q_{syn1}$</td>
<td>$(0.0131 \text{M}) 0.125 \text{ ml/min} = 0.00164 \text{ mmol/min}$</td>
</tr>
<tr>
<td>$F_{L_{A,o}} = [L_{A_{syn1}}]Q_{syn1}$</td>
<td>$(0.92 \text{ M}) 0.125 \text{ ml/min} = 0.115 \text{ mmol/min}$</td>
</tr>
<tr>
<td>$[DBU_{syn2}]$</td>
<td>$0.3 \text{ M}$</td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>$0.000493 \text{ mmol}$</td>
</tr>
<tr>
<td>$N_{brush_{max}} = 2 \frac{[L_{A_{syn1}}]}{[N_{or_{syn1}}]}$</td>
<td>$2 \frac{0.92 \text{ M}}{0.0131 \text{ M}} = 140$</td>
</tr>
<tr>
<td>$Q_{syn1}$</td>
<td>$0.125 \text{ ml/min}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$0.0254 \text{ cm}$</td>
</tr>
<tr>
<td>$L$</td>
<td>$762 \text{ cm}$</td>
</tr>
<tr>
<td>$k_{rop}$</td>
<td>$290 \frac{1}{M^{1.8} \text{ min}}$</td>
</tr>
</tbody>
</table>

The following plot was generated from the MATLAB code solving equation S33 given the inputs above.

![Figure S18: DBU flowrate for the bowtie ROP of lactide.](image-url)
Figure S19: Predicted (orange line) and experimental (blue dots) data for the bowtie ROP of lactide.

Figure S20: GPC chromatograms for the bowtie ROP of lactide.
VI. Synthesis of PLA Bottlebrush Polymers

With the output of the flow system matching the programmed profile input, the remaining steps to validate the methodology is to ensure that ROMP operates at high instantaneous conversion. The first bottlebrush synthesis will be a kinetic analysis of the bottlebrush synthesis. The second part will have the synthesis of bottlebrush from the same profiles in the previous section. The third part will be the synthesis of bottlebrushes with the same theoretical molecular weight, but different brush profiles.

![Flow system schematic](image)

**Figure S21: Schematic of the flow system for the synthesis of bottlebrushes.**

**Procedure for kinetic analysis of the bottlebrush synthesis**

In a glovebox, three solutions were generated in oven-dried glass vials:

1. lactide (1.5 g, 10.4 mmol, 0.9 mL*), norOH (18.5 mg, 0.149 mmol), 10.4 mL of THF
2. DBU (50 mg, 0.328 mmol), 1.03 mL THF
3. **B(OH)_3** (130 mg, 2.1 mmol), G3 (0.44 mg, 0.493 μmol) 4 mL of THF (20 mL vials with TFE septa)

To setup up the flow system, a 10 mL glass syringe was filled with the lactide solution, a 2.5 mL glass syringe was filled with the DBU solution, and the outlet of the flow reactor was pushed
through the septa of the B(OH)$_3$ 20 mL vial. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps, and an argon line was added to the B(OH)$_3$ vial. Once the syringes were set up, the syringe pumps were activated through the computer according to the appropriate architecture equation. At the specified time point, the syringe pump was stopped and a large excess of ethyl vinyl ether (large excess with respect to [Ru]) was immediately added to the reaction mixture. An aliquot (0.1 ml) was taken for $^1$H NMR and GPC. The rest of the reaction mixture was then poured into methanol and a centrifuge was used to isolate the resulting polymer. The polymer was dried under vacuum and then analyzed by GPC.

Notes:

*The effective volume of dissolved monomer in a 0.9 M THF solution (0.0865 ml of THF/mmol of lactide).

**In order to get B(OH)$_3$ to dissolve into THF, the solution was heated to ~110 °C till all the B(OH)$_3$ dissolved and allowed to cooled slowly back to room temperature before use. Some B(OH)$_3$ will drop out of solution. Once at room temperature, G3 was added to the mixture.

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Profile Function</th>
<th>$N_{\text{brush}}$ = 0.007$N_{bb}^2$ − 1.4$N_{bb}$ + 85</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_{\text{Nor}} = [N_{\text{or syn1}}]Q_{\text{syn1}}$</td>
<td>(0.0131M) 0.125 ml/min = 0.00164 mmol/min</td>
</tr>
<tr>
<td></td>
<td>$F_{\text{LA,0}} = [L_{\text{A syn1}}]Q_{\text{syn1}}$</td>
<td>(0.92 M) 0.125 ml/min = 0.115 mmol/min</td>
</tr>
<tr>
<td>$[\text{DBU syn2}]$</td>
<td>0.3 M</td>
<td></td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>0.000493 mmol</td>
<td></td>
</tr>
<tr>
<td>$N_{\text{syn max}} = 2 \frac{[L_{\text{A syn1}}]}{[N_{\text{or syn1}}]}$</td>
<td>$2 \frac{0.92 \text{ M}}{0.0131 \text{ M}} = 140$</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{syn1}}$</td>
<td>0.125 ml/min</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>0.0254 cm</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>762 cm</td>
<td></td>
</tr>
<tr>
<td>$k_{\text{rop}}$</td>
<td>$\frac{1}{290 M^{1.8} \text{ min}}$</td>
<td></td>
</tr>
</tbody>
</table>
Table S3: Data for the ROP of lactide during the kinetic bottlebrush synthesis

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Theory</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$ (g/mol)</td>
<td>$M_n$ (g/mol)$^a$</td>
</tr>
<tr>
<td>12</td>
<td>3010</td>
<td>3410</td>
</tr>
<tr>
<td>24</td>
<td>1440</td>
<td>1210</td>
</tr>
<tr>
<td>36</td>
<td>1420</td>
<td>1300</td>
</tr>
<tr>
<td>48</td>
<td>3010</td>
<td>2880</td>
</tr>
<tr>
<td>60</td>
<td>6260</td>
<td>5980</td>
</tr>
</tbody>
</table>

$^a$Calculated from GPC with respect to PLA standards.  
$^b$Calculated from $^1$H NMR. ND: No data

Table S4: Kinetic bottlebrush synthesis data

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>LA buildup (mmol)$^a$</th>
<th>$M_n$ (kg/mol)$^b$</th>
<th>$M_w/M_n$</th>
<th>Conv. Macro.$^c$</th>
<th>$M_n$ (kg/mol)$^a$</th>
<th>$M_n$ (kg/mol)$^d$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.78</td>
<td>180</td>
<td>0.74</td>
<td>86.4</td>
<td>1.03</td>
<td>&gt;98%</td>
<td>180</td>
<td>174</td>
<td>1.06</td>
</tr>
<tr>
<td>24</td>
<td>1.90</td>
<td>263</td>
<td>1.88</td>
<td>112</td>
<td>1.03</td>
<td>&gt;98%</td>
<td>263</td>
<td>251</td>
<td>1.09</td>
</tr>
<tr>
<td>36</td>
<td>3.12</td>
<td>314</td>
<td>2.98</td>
<td>149</td>
<td>1.03</td>
<td>&gt;98%</td>
<td>314</td>
<td>318</td>
<td>1.12</td>
</tr>
<tr>
<td>48</td>
<td>4.24</td>
<td>396</td>
<td>4.13</td>
<td>186</td>
<td>1.07</td>
<td>&gt;98%</td>
<td>396</td>
<td>399</td>
<td>1.15</td>
</tr>
<tr>
<td>60</td>
<td>5.02</td>
<td>574</td>
<td>4.95</td>
<td>250</td>
<td>1.07</td>
<td>&gt;98%</td>
<td>574</td>
<td>546</td>
<td>1.07</td>
</tr>
</tbody>
</table>

$^a$Calculated from $^1$H NMR.  
$^b$Calculated from GPC with respect to PS standards.  
$^c$The sensitivity of the NMR determined in ref.$^4$.  
$^d$Calculated from triple detection GPC

Figure S22: Predicted (orange line) and experimental GPC (blue dots) and NMR (red dots) data for the ROP of lactide during the kinetic bottlebrush synthesis.
Figure S23: Predicted (lines) and experimental (dots) molecular weight and LA buildup during the kinetic bottlebrush synthesis.

Figure S24: GPC chromatograms for the ROP of lactide during the kinetic bottlebrush synthesis.
Figure S25: NMR Spectra for the ROP of lactide during the kinetic bottlebrush synthesis.

Figure S26: GPC chromatograms of the bottlebrush kinetic aliquots.
Figure S27: $^1$H NMR spectra of the bottlebrush kinetic aliquots.

**Procedure for bottlebrush synthesis**

In a glovebox, three solutions were generated in oven-dried glass vials:

1. lactide (1.5 g, 10.4 mmol, 0.9 mL*), norOH (18.5 mg, 0.149 mmol), 10.4 mL of THF
2. DBU (50 mg, 0.328 mmol), 1.03 mL THF
3. **B(OH)$_3$** (130 mg, 2.1 mmol), G3 (0.44 mg, 0.493 μmol) 4 mL of THF (20 mL vials with TFE septa)

To set up the flow system, a 10 mL glass syringe was filled with the lactide solution, a 2.5 mL glass syringe was filled with the DBU solution, and the outlet of the flow reactor was pushed through the septa of the B(OH)$_3$ 20 mL vial. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps, and an argon line was added to the B(OH)$_3$ vial. Once the syringe pumps were set up, the syringe pumps were activated through the computer according to the appropriate profile equation. Upon completion of the addition, a large excess of
ethyl vinyl ether (large excess with respect to [Ru]) was added to the reaction mixture. An aliquot (0.1 ml) was taken for $^1$H NMR and GPC. The rest of the reaction mixture was then poured into methanol and a centrifuge was used to isolate the resulting polymer. The polymer was dried under vacuum and then analyzed by GPC.

Notes:

*The effective volume of dissolved monomer in a 0.9 M THF solution (0.0865 ml of THF/mmol of lactide).

**In order to get B(OH)$_3$ to dissolve into THF, the solution was heated to ~110 °C till all the B(OH)$_3$ dissolved and allowed to cooled slowly back to room temperature before use. Some B(OH)$_3$ will drop out of solution. Once at room temperature, G3 was added to the mixture.

The synthesis of football bottlebrush

The following is the input need for the MATLAB code.

\[
F_{Nor} = \left[ N_{or\ syn1} \right] Q_{syn1}
\]

\[
F_{LA,o} = \left[ LA_{syn1} \right] Q_{syn1}
\]

\[
[DBU_{syn2}]
\]

\[
N_{brush} = -0.007N_{bb}^2 + 1.4N_{bb}
\]

\[
(0.0131 \text{M}) \frac{0.125 \text{ml/min}}{\text{mmol/min}} = 0.00164 \text{mmol/min}
\]

\[
(0.92 \text{ M}) \frac{0.125 \text{ml/min}}{\text{mmol/min}} = 0.115 \text{mmol/min}
\]

\[
0.3 \text{ M}
\]

\[
0.000493 \text{ mmol}
\]

\[
\frac{2}{\frac{0.92}{0.0131}} = 140
\]

\[
0.125 \text{ ml/min}
\]

\[
0.0254 \text{ cm}
\]

\[
762 \text{ cm}
\]

\[
290 \frac{\frac{1}{M^{1.8}}}{\text{min}}
\]

**Table S5: Data for the synthesis of football bottlebrush**

<table>
<thead>
<tr>
<th>Architecture</th>
<th>LA buildup (mmol)</th>
<th>$M_a$ (kg/mol)</th>
<th>LA buildup (mmol)$^a$</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_a$$^b$</th>
<th>Conv. Macro.$^a,c$</th>
<th>$M_n$ (kg/mol)$^a$</th>
<th>$M_n$ (kg/mol)$^d$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>football</td>
<td>4.60</td>
<td>699</td>
<td>4.55</td>
<td>243</td>
<td>1.04</td>
<td>&gt;98%</td>
<td>699</td>
<td>640</td>
<td>1.07</td>
</tr>
</tbody>
</table>

$^a$Calculated from $^1$H NMR. $^b$Calculated from GPC with respect to PS standards $^c$The sensitivity of the NMR determined in ref.$^d$Calculated from triple detection GPC.
Figure S28: GPC chromatograms of the football bottlebrush.

Figure S29: $^1$H NMR spectrum of an aliquot from the end of the football bottlebrush synthesis.
The synthesis of bowtie bottlebrush

The following is the input need for the MATLAB code.

![Table](image)

### Table S6: Data for the synthesis of bowtie bottlebrush

<table>
<thead>
<tr>
<th>Architecture</th>
<th>LA buildup (mmol)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (kg/mol)</th>
<th>LA buildup (mmol)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (kg/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conv. Macro.</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (kg/mol)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (kg/mol)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>bowtie</td>
<td>4.60</td>
<td>698</td>
<td>4.58</td>
<td>254</td>
<td>1.05</td>
<td>&gt;98%</td>
<td>698</td>
<td>624</td>
<td>1.14</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from <sup>1</sup>H NMR.  
<sup>b</sup>Calculated from GPC with respect to PS standards.  
<sup>c</sup>The sensitivity of the NMR determined in ref.  
<sup>d</sup>Calculated from triple detection GPC.
Figure S30: GPC chromatograms of the bowtie bottlebrush.

Figure S31: $^1$H NMR spectrum of an aliquot from the end of the bowtie bottlebrush synthesis.
**Bottlebrush with identical composition**

For intrinsic viscosity measurements, bottlebrush polymers with identical chemical composition (same size, same molecular weight, same average brush length, same backbone length) were synthesized. The following details the synthesis and characterization of these samples. Both the hourglass and football synthesis were replicated five times to explore the reproducibility.

![Cylinder, hourglass, and football profile with identical composition](image)

**Figure S32: Cylinder, hourglass, and football profile with identical composition**

In a glovebox, three solutions were generated in oven-dried glass vials:

1. lactide (1.5 g, 10.4 mmol, 0.9 mL*), **norOH** (18.5 mg, 0.149 mmol), 10.4 mL of THF
2. DBU (50 mg, 0.328 mmol), 0.754 mL THF
3. **B(OH)₃** (160 mg, 2.6 mmol), **G₃** (0.44 mg, 0.493 μmol) 4 mL of THF (20 mL vials with TFE septa)

To setup up the flow system, a 10 mL glass syringe was filled with the lactide solution, a 2.5 mL glass syringe was filled with the DBU solution, and the outlet of the flow reactor was pushed through the septa of the **B(OH)₃** 20 mL vial. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps, and an argon line was added to the **B(OH)₃** vial. Once the syringe pumps were set up, the syringe pumps were activated through the computer according to the appropriate profile equation. Upon completion of the addition, a large excess of
ethyl vinyl ether (large excess with respect to [Ru]) was added to the reaction mixture. An aliquot (0.1 ml) was taken for $^1$H NMR and GPC. The rest of the reaction mixture was then poured into methanol and a centrifuge was used to isolate the resulting polymer. The polymer was dried under vacuum and then analyzed by GPC.

Notes:

*The effective volume of dissolved monomer in a 0.9 M THF solution (0.0865 ml of THF/mmol of lactide).

**In order to get B(OH)$_3$ to dissolve into THF, the solution was heated to ~110 °C till all the B(OH)$_3$ dissolved and allowed to cooled slowly back to room temperature before use. Some B(OH)$_3$ will drop out of solution. Once at room temperature, G3 was added to the mixture.

The synthesis of cylindrical bottlebrush (compositionally identical)

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile Function</td>
<td>$N_{brush} = 50$</td>
</tr>
<tr>
<td>$F_{Nor} = \left[ N_{or\ syn1} \right] Q_{syn1}$</td>
<td>(0.0131M) 0.125 ml/min= 0.00164 mmol/min</td>
</tr>
<tr>
<td>$F_{LA,0} = \left[ LA_{syn1} \right] Q_{syn1}$</td>
<td>(0.92 M) 0.125 ml/min= 0.115 mmol/min</td>
</tr>
<tr>
<td>$\left[ DBU_{syn2} \right]$</td>
<td>0.4 M</td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>0.000493 mmol</td>
</tr>
<tr>
<td>$N_{syn max}^{brush} = 2 \frac{[LA_{syn1}]}{[N_{or\ syn1}]}$</td>
<td>$= 2 \frac{0.92 \text{ M}}{0.0131 \text{ M}} = 140$</td>
</tr>
<tr>
<td>$Q_{syn1}$</td>
<td>0.1 ml/min</td>
</tr>
<tr>
<td>$R$</td>
<td>0.0254 cm</td>
</tr>
<tr>
<td>$L$</td>
<td>762 cm</td>
</tr>
<tr>
<td>$k_{rop}$</td>
<td>$= 290 \frac{1}{M^{1.8} \text{ min}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Architecture</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>Conv. Macro.</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder</td>
<td>4.44</td>
<td>744</td>
<td>4.49</td>
<td>265</td>
<td>1.03</td>
<td>&gt;98%</td>
<td>744</td>
<td>768</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Table S7: Data for the synthesis of cylindrical bottlebrush (compositionally identical)

*aCalculated from $^1$H NMR. bCalculated from GPC with respect to PS standards. cThe sensitivity of the NMR determined in ref. 4. dCalculated from triple detection GPC.

** At the end of the flow run, the tubular reactor was pulled out of the vial and an aliquot was taken for GPC. $M_n= 3,700$ g/mol, $N_{PLA}=49.5$, $M_w/M_n=1.05$. 

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Figure S33: GPC chromatograms of the cylindrical bottlebrush with brush aliquot (orange trace).

Figure S34: $^1$H NMR spectrum of an aliquot from the end of the cylindrical bottlebrush synthesis.
The synthesis of hourglass bottlebrush (compositionally identical)

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>hourglass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile Function</td>
<td>$N_{\text{brush}} = 0.0075 N_{\text{br}}^2 - 1.5 N_{\text{bb}} + 100$</td>
</tr>
<tr>
<td>$F_{\text{Nor}} = \left[ N_{\text{or syn1}} \right] Q_{\text{syn1}}$</td>
<td>(0.0131M) 0.125 ml/min = 0.00164 mmol/min</td>
</tr>
<tr>
<td>$F_{\text{LA.o}} = \left[ L_{\text{A syn1}} \right] Q_{\text{syn1}}$</td>
<td>(0.92 M) 0.125 ml/min = 0.115 mmol/min</td>
</tr>
<tr>
<td>$\left[ DBU_{\text{syn2}} \right] = 0.4 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>0.000493 mmol</td>
</tr>
<tr>
<td>$N_{\text{syn max}} = 2 \frac{[L_{\text{A syn1}}]}{[N_{\text{or syn1}}]}$</td>
<td>$2 \frac{0.92 \text{ M}}{0.0131 \text{ M}} = 140$</td>
</tr>
<tr>
<td>$Q_{\text{syn1}}$</td>
<td>0.1 ml/min</td>
</tr>
<tr>
<td>$R$</td>
<td>0.0254 cm</td>
</tr>
<tr>
<td>$L$</td>
<td>762 cm</td>
</tr>
<tr>
<td>$k_{\text{rop}}$</td>
<td>$290 \frac{1}{M^{1.8} \text{ min}}$</td>
</tr>
</tbody>
</table>

Table S8: Data for the synthesis of hourglass bottlebrush (compositionally identical)

<table>
<thead>
<tr>
<th>Sample</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>LA buildup (mmol)$^a$</th>
<th>$M_n$ (kg/mol)$^b$</th>
<th>$M_w/M_n$</th>
<th>Conv. Macro.$^{a,c}$</th>
<th>$M_n$ (kg/mol)$^a$</th>
<th>$M_w$ (kg/mol)$^d$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.44</td>
<td>744</td>
<td>4.47</td>
<td>286</td>
<td>1.05</td>
<td>&gt;98%</td>
<td>744</td>
<td>793</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>4.34</td>
<td>744</td>
<td>4.34</td>
<td>291</td>
<td>1.08</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>4.56</td>
<td>291</td>
<td>4.56</td>
<td>291</td>
<td>1.07</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>4.30</td>
<td>287</td>
<td>4.30</td>
<td>287</td>
<td>1.08</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>4.42</td>
<td>282</td>
<td>4.42</td>
<td>282</td>
<td>1.09</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>4.42</td>
<td>287</td>
<td>4.42</td>
<td>287</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Calculated from $^1$H NMR. $^b$Calculated from GPC with respect to PS standards. $^c$The sensitivity of the NMR determined in ref.$^d$Calculated from triple detection GPC.
Figure S35: GPC chromatograms of the hourglass bottlebrush

Figure S36: $^1$H NMR spectrum of an aliquot from the end of the hourglass bottlebrush synthesis.
The synthesis of football bottlebrush (compositionally identical)

The following is the input need for the MATLAB code.

\[
N_{\text{brush}} = -0.0075 N_{bb}^2 + 1.5 N_{bb}
\]

\[
F_{\text{Nor}} = [N_{\text{or syn1}}] Q_{\text{syn1}} \quad (0.0131 \text{M}) \quad 0.125 \text{ ml/min} = 0.00164 \text{ mmol/min}
\]

\[
F_{\text{LA.o}} = [L_{\text{A syn1}}] Q_{\text{syn1}} \quad (0.92 \text{ M}) \quad 0.125 \text{ ml/min} = 0.115 \text{ mmol/min}
\]

\[
[\text{DBU}_{\text{syn2}}] = 0.4 \text{ M}
\]

\[
n_{\text{G3}} = 0.000493 \text{ mmol}
\]

\[
N_{\text{syn max}} = 2^{\frac{[L_{\text{A syn1}}]}{[N_{\text{or syn1}}]}} \quad 2^{\frac{0.92}{0.0131}} = 140
\]

\[
Q_{\text{syn1}} = 0.1 \text{ ml/min}
\]

\[
R = 0.025 \text{ cm}
\]

\[
L = 762 \text{ cm}
\]

\[
k_{\text{rop}} = 290 \frac{1}{M^{1.8} \text{ min}}
\]

Table S9: Data for the synthesis of football bottlebrush (compositionally identical)

<table>
<thead>
<tr>
<th>Sample</th>
<th>LA buildup (mmol)</th>
<th>M_n (kg/mol)</th>
<th>LA buildup (mmol)^a</th>
<th>M_n (kg/mol)</th>
<th>M_w/M_n</th>
<th>Conv. Macro. a,c</th>
<th>M_n (kg/mol)</th>
<th>M_w/M_n</th>
<th>M_w/M_n d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.44</td>
<td>4.48</td>
<td>249</td>
<td>1.04</td>
<td>&gt;98%</td>
<td>744</td>
<td>811</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>4.36</td>
<td>249</td>
<td>1.06</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>4.46</td>
<td>241</td>
<td>1.04</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>4.25</td>
<td>242</td>
<td>1.05</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>4.39</td>
<td>249</td>
<td>1.08</td>
<td>&gt;98%</td>
<td>744</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>4.39</td>
<td>246</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

^aCalculated from ^1^H NMR. ^bCalculated from GPC with respect to PS standards. ^cThe sensitivity of the NMR determined in ref. ^dCalculated from triple detection GPC.
Figure S37: GPC chromatograms of the football bottlebrush

Figure S38: $^1$H NMR spectrum of an aliquot from the end of the football bottlebrush synthesis.
**Bottlebrush via inverse design**

The inverse design route was used to synthesis the double sphere bottlebrush profile. The design or molecular geometry was set as the target for the inverse design protocol (see section XI). From the inverse design protocol, the brush profile was obtained and two fourth order polynomials were fit to the data. The two polynomials will be combined in a piece-wise function and used as the input into the MATLAB code (see section XII).

\[ N_{brush} = \begin{cases} 
4.977 \times 10^{-6} N_{bb}^4 - 0.001016 N_{bb}^3 + 0.04072 N_{bb}^2 + 1.127 N_{bb} + 11 & 0 \leq N_{bb} \leq 100 \\
5.268 \times 10^{-6} N_{bb}^4 - 0.003161 N_{bb}^3 + 0.6735 N_{bb}^2 - 59.78 N_{bb} + 1889 & 101 \leq N_{bb} \leq 200 
\end{cases} \]

**Figure S39: Schematic of the inverse design to obtain brush profile function**

In a glovebox, three solution were generated in oven-dried glass vials:

1. lactide (1.5 g, 10.4 mmol, 0.9 mL*), norOH (18.5 mg, 0.149 mmol), 10.4 mL of THF
2. DBU (50 mg, 0.328 mmol), 0.348 mL THF
3. **B(OH)₃ (160 mg, 2.6 mmol), G3 (0.44 mg, 0.493 μmol) 4 mL of THF (20 mL vials with TFE septa)

To setup up the flow system, a 10 mL glass syringe was filled with the lactide solution, a 2.5 mL glass syringe was filled with the DBU solution, and the outlet of the flow reactor was pushed
through the septa of the B(OH)$_3$ 20 mL vial. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps, and an argon line was added to the B(OH)$_3$ vial. Once the syringe pumps were set up, the syringe pumps were activated through the computer according to the appropriate profile equation. Upon completion of the addition, a large excess of ethyl vinyl ether (large excess with respect to [Ru]) was added to the reaction mixture. An aliquot (0.1 ml) was taken for $^1$H NMR and GPC. The rest of the reaction mixture was then poured into methanol and a centrifuge was used to isolate the resulting polymer. The polymer was dried under vacuum and then analyzed by GPC.

Notes:

*The effective volume of dissolved monomer in a 0.9 M THF solution (0.0865 ml of THF/mmol of lactide).

**In order to get B(OH)$_3$ to dissolve into THF, the solution was heated to ~110 °C till all the B(OH)$_3$ dissolved and allowed to cooled slowly back to room temperature before use. Some B(OH)$_3$ will drop out of solution. Once at room temperature, G3 was added to the mixture.

The following is the input need for the MATLAB code.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Double sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profile Function</td>
<td>See above</td>
</tr>
<tr>
<td>$F_{Nor} = [Nor_{syn1}]Q_{syn1}$</td>
<td>(0.0131M) 0.0938 ml/min = 0.00122 mmol/min</td>
</tr>
<tr>
<td>$F_{LA,o} = [LA_{syn1}]Q_{syn1}$</td>
<td>(0.92 M) 0.0938 ml/min = 0.0863 mmol/min</td>
</tr>
<tr>
<td>$[DBU_{syn2}]$</td>
<td>0.8 M</td>
</tr>
<tr>
<td>$n_{G3}$</td>
<td>0.000493 mmol</td>
</tr>
<tr>
<td>$N_{max}^{syn} = 2 \frac{[LA_{syn1}]}{[Nor_{syn1}]}$</td>
<td>$2 \frac{0.92 M}{0.0131 M} = 140$</td>
</tr>
<tr>
<td>$Q_{syn1}$</td>
<td>0.0938 ml/min</td>
</tr>
<tr>
<td>$R$</td>
<td>0.0254 cm</td>
</tr>
<tr>
<td>$L$</td>
<td>762 cm</td>
</tr>
<tr>
<td>$k_{rop}$</td>
<td>$290 \frac{1}{M^{1.8} \text{min}}$</td>
</tr>
</tbody>
</table>
Table S10: Data for the synthesis of double sphere bottlebrush via inverse design

<table>
<thead>
<tr>
<th>Architecture</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>LA buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>Conv. Macro.</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double sphere</td>
<td>4.49</td>
<td>732</td>
<td>4.42</td>
<td>242</td>
<td>1.06</td>
<td>&gt;98%</td>
<td>732</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calculated from $^1$H NMR. $^b$Calculated from GPC with respect to PS standards. $^c$The sensitivity of the NMR determined in ref.$^4$. $^d$Calculated from triple detection GPC.

Figure S40: GPC chromatograms of the double sphere bottlebrush
Figure S41: \(^1\)H NMR spectrum of an aliquot from the end of the double sphere bottlebrush synthesis via inverse design.

VII. Atomic Force Microscopy Images
Atomic force microscopy (AFM) imaging was performed using a MFP-3D system (Asylum Research, Santa Barbara, CA) in tapping mode using standard silicon tips (Tap150Al-G tips, F: 150 kHz, C: 5 N/m, L: 125 μm, Budget Sensors). Samples were prepared by spin casting dilute solutions (ca. 0.002 mg/mL) of bottlebrush in chloroform onto freshly functionalized Si wafers. Functionalized Si wafers were made by cleaning the surface with THF and toluene, then plasma treated for 5 minutes before immediately plunging the wafer in a TMSCl/toluene solution. The wafers were left in the TMSCl solution for 24 h before drying under a flow nitrogen, and coated with the dilute solution of bottlebrush. Samples were analyzed by AFM within 2 hours after preparation.

The theoretical profile was calculated based on the profile equation and the lengths of each repeat unit’s length.\(^4\) (Norbornene=0.625 nm; lactide= 0.365 nm)
Hourglass (compositionally identical) samples

Figure S42: Height map of hourglass bottlebrush polymers

Figure S43: Zoomed-in height map of hourglass bottlebrush polymers
Figure S44: Height map of hourglass bottlebrush polymers

Figure S45: Normalized height profiles of hourglass bottlebrush polymers with theoretical profile (blue line)
Hourglass (compositionally identical) samples

Figure S46: Normalized height profiles of football bottlebrush polymers with theoretical profile (blue line)

VIII. Ring Opening Polymerization of δ-Valerolactone (Flow)

For the development of the valerolactone chemistry in the flow system, we wanted to demonstrate and alterative approach that does not require the rate law which can be time consuming to develop. This approach simply runs the flow system at various different TBD flow rates and quantifies the output. From that, we can directly map the brush length to a TBD flow rate for any desired architecture bottlebrush.
Ring opening polymerization of valerolactone with different TBD flow rates

![Diagram of flow system](image)

Figure S47: Schematic of the flow system for the ROP of valerolactone

Ring opening polymerization of δ-valerolactone with TBD in batch was originally reported in literature. In a glovebox, two solutions were generated in oven-dried glass vials:

1. δ-Valerolactone (3.6 g, 36 mmol, 3.33 mL), octanol (15.6 mg, 0.120 mmol), 8.6 mL of THF
2. TBD (60 mg, 0.43 mmol), 1.0 mL THF

To setup up the flow system, a 10 mL glass syringe was filled with the δ-valerolactone solution, and a 2.5 mL glass syringe was filled with the TBD solution. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps. Once the syringe pumps were set up, the syringe pumps were activated through the computer. Once liquid began exiting the tube, samples were taken by collecting 2 drops (~15 μL) of the reaction mixture in a vial of 0.1 M acetic acid in THF or CDCl₃. The samples were then analyzed by GPC and/or NMR.
Table S11: Flow rates for the flow experiment

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (min)</th>
<th>VL Flow (ml/min)</th>
<th>TBD Flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0→10</td>
<td>0.1310</td>
<td>3.37</td>
</tr>
<tr>
<td>2</td>
<td>10→20</td>
<td>0.1310</td>
<td>0.60</td>
</tr>
<tr>
<td>3</td>
<td>20→30</td>
<td>0.1310</td>
<td>4.60</td>
</tr>
<tr>
<td>4</td>
<td>30→40</td>
<td>0.1310</td>
<td>2.25</td>
</tr>
<tr>
<td>5</td>
<td>40→50</td>
<td>0.1310</td>
<td>5.96</td>
</tr>
</tbody>
</table>

Figure S48: Brush length results from the TBD flow rate sweep
Figure S49: GPC traces for the TBD flow rate sweep

Figure S50: $^1$H NMR spectra for the TBD flow rate sweep
The data form Figure S48 can be converted into Figure S51. Then any function can be fitted to the data. In this case, a linear line appeared to fit the data quite well. The fit will be used in the following section to determine the TBD flow rate for a desired profile.

Figure S51: $^1$H NMR spectra for the TBD flow rate sweep

\[
(TBD \text{ flow rate}) = 7.137 \times 10^{-5}N_{brush} + 2.383 \times 10^{-5}
\]  

Ring opening polymerization of valerolactone for the a sphere

The target bottlebrush architecture will be a sphere. Thus, the contour is a circle. The general equation for a circle is shown below.

\[
(x - h)^2 + (y - k)^2 = r^2
\]

To convert the circle equation into a bottlebrush profile, we will take \( x = N_{bb} \) and \( y = N_{brush} \). We will target a radius of 50.

\[
(N_{bb} - 50)^2 + N_{brush}^2 = 50^2
\]

Then rearranging for \( N_{brush} \) and ignoring the negative component gives:

\[
N_{brush} = \sqrt{50^2 - (N_{bb} - 50)^2}
\]

To obtain a TBD flow rate equation, equation S35 can be plugged into equation S34.

\[
(TBD \text{ flow rate}) = 7.137 \times 10^{-5}\sqrt{50^2 - (N_{bb} - 50)^2} + 2.383 \times 10^{-5}
\]

Finally, to get a TBD flow rate versus time equation, equation S15 will be used to convert \( N_{bb} \) to time.
\[
(TBD \text{ flow rate}) = 7.137 \times 10^{-5} \sqrt{50^2 - \left(\left[\frac{I_{\text{syn1}}}{Q_{\text{syn1}} t_{\text{bb,cat}}}\right] - 50\right)^2} + 2.383 \times 10^{-5}
\]

\[I_{\text{syn1}} = 0.01 \text{ M}\]

\[Q_{\text{syn1}} = 0.131 \text{ ml/min}\]

\[n_{\text{bb,cat}} = 0.8 \mu\text{mol}\]

Figure S52: TBD flow rate profile for a sphere bottlebrush

Figure S53: Predicted (orange line) and experimental (GPC: blue dots; NMR: red dots) data for the sphere ROP of valerolactone.
Figure S54: GPC chromatograms for the sphere ROP of valerolactone.
**Figure S55: **$^1$H NMR spectra for the sphere ROP of valerolactone.

**IX. Synthesis of PVL Bottlebrush Polymers**
In the previous section, a relationship between TBD flow rate and brush length was determined for the ring opening polymerization of valerolactone. In this section that function will be used to synthesize an architecture-controlled bottlebrush polymer.
The procedure for the synthesis of PVL bottlebrush polymers

In a glovebox, three solution were generated in oven-dried glass vials:

1. δ-Valerolactone (3.6 g, 36 mmol, 3.33 mL), norOH (14.9 mg, 0.120 mmol), 8.6 mL of THF
2. TBD (60 mg, 0.43 mmol), 1.0 mL THF
3. *B(OH)$_3$ (87 mg, 1.4 mmol), G3 (0.71 mg, 0.80 μmol) 4 mL of THF (20 mL vials with TFE septa)

To setup up the flow system, a 10 mL glass syringe was filled with the δ-valerolactone solution, a 2.5 mL glass syringe was filled with the TBD solution and the outlet of the was pushed through the septa of the B(OH)$_3$ 20 mL vial. The entire flow setup was taken out of the glovebox, placed into the computer controlled syringe pumps, and an argon line was added to the B(OH)$_3$ vial. Once the syringe pumps were set up, the syringe pumps were activated through the computer according to the appropriate profile equation. Upon completion of the addition, a large excess of ethyl vinyl ether (large excess with respect to [Ru]) was added to the reaction mixture. The reaction mixture was then poured into 300 mL of methanol and a centrifuge was used to isolate the resulting polymer. The polymer was dried under vacuum.
Notes:

*In order to get B(OH)$_3$ to dissolve into THF, the solution was heated to ~110 °C till all the B(OH)$_3$ dissolved and allowed to cooled slowly back to room temperature before use. Some B(OH)$_3$ will drop out of solution. Once at room temperature, G3 was added to the mixture.

### Calculation for $M_n$ and VL buildup

Both $M_n$ and VL can be calculated by integrating the architecture equation S35 and dividing by the backbone length to give the average brush length (or in this special case: by calculating the area of a circle with a radius of 50, dividing by 2 and backbone length (Area=(π $50^2)/2/N_{bb}$)).

$$N_{brush_{avg}} = \int_0^{N_{bb}} \sqrt{50^2 - (N'_{bb} - 50)^2} \, dN'_{bb} / N_{bb} = \frac{1}{100} \int_0^{100} \sqrt{50^2 - (N'_{bb} - 50)^2} \, dN'_{bb}$$

$$N_{brush_{avg}} = \frac{1}{100} \left[ 1250 \cdot \sin^{-1}\left(\frac{N_{bb} - 50}{50}\right) + \frac{(N_{bb} - 50)\sqrt{-N_{bb}(N_{bb} - 100)}}{2} \right]_{0}^{100}$$

$$N_{brush_{avg}} = \frac{25\pi}{2} \approx 39.3$$

The backbone bottlebrush molecular weight is calculated by the average brush length times the backbone length plus the backbone molecular weight.

$$M_{n, BB} = \left( N_{brush_{avg}} \cdot MW_{brush-unit} + MW_{backbone-unit} \right) N_{bb}$$

$$M_{n, BB} = (39.3 \left( 100.12 \frac{g}{mol} \right) + 124 \frac{g}{mol}) 100 = 406 \, kg/mol$$

To calculate VL buildup, multiply the unreacted VL times the moles of VL that is feed into the ROMP pot over the entire bottlebrush synthesis.

$$VL_{buildup} = \left( 1 - \frac{N_{brush_{avg}}}{N_{brush}} \right) \cdot \text{(mmol of VL pushed into the ROMP pot)}$$

$$VL_{buildup} = \frac{39.3}{300} \cdot 24 \, mmol = 20.86 \, mmol$$

### Table S12: Data for the synthesis of PVL bottlebrush

<table>
<thead>
<tr>
<th>Architecture</th>
<th>VL buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>VL buildup (mmol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>Conv.</th>
<th>Macro.</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>20.86</td>
<td>406</td>
<td>20.90</td>
<td>130</td>
<td>1.05</td>
<td>&gt;98%</td>
<td></td>
<td>406</td>
<td>379</td>
<td>1.05</td>
</tr>
</tbody>
</table>

*Calculated from $^1$H NMR. $^b$Calculated from GPC with respect to PS standards $^c$The sensitivity of the NMR determined in ref. $^d$Calculated from triple detection GPC.
Figure S57: GPC chromatogram for the synthesis of PVL bottlebrush

Figure S58: $^1$H NMR spectra for the synthesis of PVL bottlebrush
X. Intrinsic Viscosity

Samples were prepared by dissolving the bottlebrush with filtered (0.22 μm pores) THF to form a concentrated bottlebrush solution. The concentrated bottlebrush solution was then divided in 5 dilute samples ranging in concentration from 4-12 mg/ml. Each dilute solution was measured by a Cannon-Fenske glass capillary viscometer (viscometer constant ~ 0.004 cSt/s) at 30 °C. The intrinsic viscosity $[\eta]$ was determined by fitting to the Huggins model. Plot $\eta_{sp}/c$ vs. $c$ and the intercept is $[\eta]$.

Huggins’ equation

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\eta_{solution}}{c} - 1 = \lim_{c \to 0} \frac{\Delta t_{solution}}{\Delta t_{solvent}} - 1$$

See Section VI for details on the synthesis and characterization of the compositionally identical bottlebrushes.

Table S13: Intrinsic viscosity data

<table>
<thead>
<tr>
<th>Architecture</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_n/M_w$</th>
<th>$[\eta]$ dL/g</th>
<th>ratio</th>
<th>$[\eta]$ dL/g</th>
<th>ratio</th>
<th>$[\eta]$ dL/g</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hourglass</td>
<td>793</td>
<td>1.10</td>
<td>0.433</td>
<td>1.12</td>
<td>0.437</td>
<td>1.14</td>
<td>0.378</td>
<td>1.08</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>768</td>
<td>1.03</td>
<td>0.387</td>
<td>1</td>
<td>0.382</td>
<td>1</td>
<td>0.349</td>
<td>1</td>
</tr>
<tr>
<td>Football</td>
<td>811</td>
<td>1.05</td>
<td>0.318</td>
<td>0.82</td>
<td>0.360</td>
<td>0.94</td>
<td>0.282</td>
<td>0.81</td>
</tr>
</tbody>
</table>

$^a$THF, 30 °C $^b$With respect to cylinder $[\eta]$ $^c$ t-GPC $^d$ THF, 35 °C

Figure S59: Data for the calculation of intrinsic viscosity.
XI. Simulation Model and Method

Model
Bottlebrush polymers are represented using a bead-spring model. The backbone consists of $N_{bb}$ beads, and each backbone bead carries a side chain consisting of $N_{sc}$ beads. Connectivities between the beads are implemented via finitely extensible nonlinear elastic (FENE) springs. The spring potential between two connected beads $i$ and $j$ is

$$U_s = -\frac{1}{2} k_s r_{ij}^2 \ln \left[ 1 - \left( \frac{r_{ij}}{r_{max}} \right)^2 \right], \quad r_{ij} < r_{max},$$

where $k_s = 30\varepsilon/\sigma^2$ is the spring constant, $r_{max} = 1.5\sigma$ is the maximum extensible spring length, and $r_{ij}$ is the distance between the beads.\(^6\) Here, $\sigma$ is the length parameter and $\varepsilon$ is the energy parameter (in unit of $k_B T$; $k_B$ being the Boltzmann factor and $T$ the absolute temperature).

Excluded volume interaction among the beads is implemented by the pairwise Weeks-Chandler-Anderson (WCA) potential\(^7\)

$$U_{ev} = \begin{cases} 4 \varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] - 4 \varepsilon \left[ \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^{6} \right], & r_{ij} < r_c \\ 0, & \text{otherwise,} \end{cases}$$

where $r_c = 2^{1/6} \sigma$. This form of $U_{ev}$ models a bottlebrush under athermal condition. In addition, a bending potential of the form

$$U_b = \frac{1}{2} k_B T \left( 1 - \cos \theta_{ij} \right)$$

is introduced only along the backbone, where $\theta_{ij} = \cos^{-1} (\mathbf{u}_i \cdot \mathbf{u}_j)$ is the bond angle (complementary) between the unit vectors along consecutive backbone bonds. The parameterization of this model for a PNB-PLA bottlebrush has been discussed in detail in reference.\(^8\) Here, we simply mention that the length parameter $\sigma = 0.67$ nm, the backbone molecular weight (in Da) $M_{bb} = 134.6 (N_{bb} - 1)$, the side chain molecular weight (in Da) $M_{sc} = 161.8 (N_{sc} - 1)$, and the total molecular weight $M = 134.6 (N_{bb} - 1) + 161.8N_{sc}N_{bb}$. 
Method for a fixed architecture

We use standard metropolis Monte Carlo (MC) method to sample equilibrium conformations of a bottlebrush molecule. The MC moves include local bead displacement, crankshaft, and pivot. Crankshaft moves are employed locally on the side chain beads, while an $n$-point (with $n$ chosen randomly) version capable of introducing global conformational changes is used for the backbone. The pivot moves have two variants — one operating on the backbone as a whole, while the other operating on individual side chains.

Each MC cycle consists of $N/2$ bead displacement moves, $N/2$ local crankshaft moves (on side chain beads), $N_s/2$ side chain pivot moves, a single backbone pivot move, and a single backbone $n$-point crankshaft move, where $N$ is the total number of beads and $N_s$ is the total number of side chains. Each MC run consists of six independent trajectories, each trajectory being at least $1 \times 10^6$ cycles long. The first $1 \times 10^5$ cycles of each trajectory are considered as the equilibration stage and discarded for calculating properties based on the conformations.

We calculate the intrinsic viscosity $[\eta]$ using the expression:

$$[\eta] = \frac{5 N_A V_1}{2 M_1} + \frac{N_A}{6 M_1 \eta_s} \left( \frac{\zeta \sum_i R_i^2}{1 + \frac{\zeta Q}{8 \pi \eta_s \sum_i R_i^2}} \right),$$

where $\zeta = 3 \pi \eta_s \sigma$ is the friction coefficient of a bead, $N_A$ is the Avogadro number, $V_1 = \pi \sigma^3/6$ is the volume of a bead, $M_1$ is the molar mass of a bead, and

$$Q = \sum_l \sum_{s \neq l} \left[ \frac{R_l \cdot R_s}{R_{ls}} + \frac{1}{10 R_{ls}^3} \left\{ 4(R_l^2 + R_s^2)R_l \cdot R_s - R_l^2 R_s^2 - 7(R_l \cdot R_s)^2 \right\} \right],$$

where $R_l$ is the position vector of bead $l$ with respect to the molecule center-of-mass, $R_l = \|R_l\|$, and $R_{ls} = \|R_s - R_l\|$. The expression for intrinsic viscosity was originally derived by Tsuda using a non-preaveraged version of Kirkwood theory for rigid molecules; later work by de la Torre and coworkers adapted that for application to flexible macromolecules. Although the expression for intrinsic viscosity contains several approximations, we have verified in our earlier publication that for linear polymers it indeed reproduces mass-scaling as expected from Zimm theory in dilute solution.
**Method for profile optimization**

We assume that a target profile has been provided; the goal is to determine the number of beads for each side chain that will generate the target profile at equilibrium. We identify the thickness of the bottlebrush along the backbone with the radius of gyration of the side chain grafted at that location. To this end, we start from the bare backbone and iteratively add or remove beads on each side chain to approach the target profile.

During the first iteration, the bare backbone is relaxed to equilibrium (the number of side chain beads are zero at this stage). For each subsequent iteration, whether beads are to be added onto or removed from each side chain is determined based on an error function $E(i) = S_T(i) - S(i)$, where $S_T(i)$ and $S(i)$ are the target and current radius of gyration of the $i^{th}$ side chain, respectively. The number of beads to be added or removed for any side chain $i$ is determined from the expression

$$\Delta S^2(i) = b^2 \Delta N(i)/6,$$

where $\Delta S^2(i) = S_T^2(i) - S^2(i)$ and $b = 0.97\sigma$ is the equilibrium bond length and $N(i)$ is the number of beads in side chain $i$. Within each iteration, we equilibrate the structure and carry out a production run as described in the previous section, though the number of cycles is shorter for these iterating runs. For each side chain, $S(i)$ is calculated by averaging over the entire production run for the current iteration. The residual $R = \max |E(i)|$, where $S_T(i)$ and $S(i)$ are the target and current radius of gyration of the $i^{th}$ side chain, respectively, controls the number of iterations. If $R$ is less than some prespecified tolerance (typically one bond length), the iterations are stopped.

Figure S57 shows the profile and side chain DP along the backbone for different iterations for an example case of $N_{bb} = 200$. 


Figure S57: (left) Side chain radius of gyration (profile) as a function of backbone bead index for different iterations. (right) Side chain DP (number of beads) corresponding to each iteration shown in the left panel.

XII. MATLAB Code to Solve Flow Rate Equation
The following MATLAB code was written to solve equation S33. The MATLAB code utilizes the secant method to solve the equation.

The code:

```matlab
function Calculating_DBU_flowrate
close all; clear all; clc
%% Inputs %%
% Profile
Profile_op=1; % l=function 0=piece-wise funtion(see imput at very bottom of script)
Profile_fun=@(x) 0.0075*x^2-1.5*x+100; % profile function
N_brush(Nbb)=Profile_fun(x)
% Reactions Conditions
Nor_con=0.0131; %[M]
LA_con=0.92; %[M]
DBU_con=0.4; %[M]
n_G3=0.000493; %mmole
Q_syn1=0.1; %ml/min
F_Nor=Nor_con*Q_syn1; %mmol/min
F_LA=LA_con*Q_syn1; %mmol/min
N_brush_syn_max=LA_con/Nor_con*2;
Flow_vol=7.5; %ml
% Reactor details
R=0.0254; %cm
L=762; %cm
% Time Inputs
```
flow_time = Flow_vol/Q_syn1; % min
n = 100; % simulations points per min

% Chemistry Inputs
Chemistry = 1; % 1=PLA  2=PVL
if Chemistry == 1
    kp = 290; % 1/(min M^2)
    brush_repeat_MW = 72.2;
else
    kp = 290; % PVL 1/(min M^2)
    brush_repeat_MW = 100; % Valerolactone
end
Nor_repeat_MW = 124.2;

% Plotting options
op_MW_plots = 1; % 1=MW Plots 0= No MW plots
op_save_plots = 0; % 1=save plots and excel file 0=no saving

%% Calculations %
fprintf('Starting calculations 
 n----------------------
 n')

% General Calculations
Tube_Vol = pi*R^2*L;
Mn_brush_syn_max = N_brush_syn_max*brush_repeat_MW + Nor_repeat_MW;
N_bb_syn_max = F_Nor*flow_time/n_G3;

% Time calculations
npts = (flow_time+5)*n; % Number of points in simulation
t = linspace(0,flow_time+5,npts); % Time vector
dt = t(1,2) - t(1,1); % time between points
[~, t_end_DBU_i] = min(abs(t(1,:)-flow_time));

% DBU flow rate calculations
N_bb = linspace(0,N_bb_syn_max,t_end_DBU_i); N_brush = zeros(1,t_end_DBU_i);
if Profile_op == 1
    for i = 1:t_end_DBU_i
        N_brush(1,i) = feval(Profile_fun,N_bb(1,i));
    end
else
    for i = 1:t_end_DBU_i
        N_brush(1,i) = Profile_fun_piecewise(N_bb(1,i));
    end
end
t_flow = n_G3/(Nor_con*Q_syn1)*N_bb;
DBU_flow_rate = zeros(1,t_end_DBU_i);
f_nor = Nor_con*Q_syn1;
f_lac_o = LA_con*Q_syn1;
R = 5;
k = 1; a = 0.0001; b = 0.00011;
for i = 1:t_end_DBU_i
    if N_brush(1,i) == 0;
        DBU_flow_rate(1,i) = 0;
    else
        if k < 3
            DBU_flow_rate(1,i) = Root_finder_secant(a,b,Q_syn1,dbu_con,kp,f_nor,Tube_Vol,dbu
            brush(1,i),N_brush_syn_max,f_lac_o);
            k = k+1;
        else
            if DBU_flow_rate(1,i-1) == DBU_flow_rate(1,i-2)
            else
            end
        end
    end
end
DBU_flow_rate(1,i)=Root_finder_secant(DBU_flow_rate(1,i-1)+a,DBU_flow_rate(1,i-2),Q_syn1,DBU_con,kp,f_nor,Tube_Vol,N_brush(1,i),N_brush_syn_max,f_lac_o);
else
    DBU_flow_rate(1,i)=Root_finder_secant(DBU_flow_rate(1,i-1),DBU_flow_rate(1,i-2),Q_syn1,DBU_con,kp,f_nor,Tube_Vol,N_brush(1,i),N_brush_syn_max,f_lac_o);
end
end
end
[max_DBU_flow_rate,~]=max(DBU_flow_rate);

% Lactide Buildup and BB MW
Lac_in_pot=zeros(1,t_end_DBU_i); Lac_MW=zeros(1,t_end_DBU_i);
BB_MW=zeros(1,t_end_DBU_i);
for i=2:t_end_DBU_i
    Lac_in_pot(1,i)=Lac_in_pot(1,i-1)+LA_con*Q_syn1*dt*(1-N_brush(1,i)/N_brush_syn_max);
    Lac_MW(1,i)=Lac_MW(1,i-1)+(N_bb(1,2)-N_bb(1,1))*(N_brush(1,i)+N_brush(1,i-1))/2*brush_repeat_MW;
    BB_MW(1,i)=Lac_MW(1,i)+N_bb(1,i)*Nor_repeat_MW;
end

%output text
fprintf('
Synthetic Maximums

N_brush = %2.2f 	 Mn_brush = %2.2f

N_backbone = %2.2f

Reactor and flow rates

R=%2.3f cm, L=%2.2f cm

Flow rate of Nor&Lac = %2.3f ml/min 	 [flow time= %2.2f min]

Max Flow rate of DBU = %2.4f ml/min 	 [Max S2/S1= %2.1f %]

Max DBU flow rate, max(DBU_flow_rate/Q_syn1*100)

Bottlebrush polymer calculations'
fprintf('
Max Brush length = %2.1f | %4.0f g/mol',max(N_brush),max(N_brush)*brush_repeat_MW+Nor_repeat_MW)
fprintf('
Mean Brush length = %2.1f | %4.0f g/mol',mean(N_brush),mean(N_brush)*brush_repeat_MW+Nor_repeat_MW)
fprintf('
BB MW(1,end) = %6.0f g/mol',BB_MW(1,end))
fprintf('Lactide buildup = %1.2f mmol(%2.1f %)',Lac_in_pot(1,end),Lac_in_pot(1,end)/(F_LA*flow_time)*100)

% Plotting
f1=figure;
subplot(1,3,1)
hold on
plot(N_bb,N_brush,'b-','LineWidth',3)
%% Saving %
if op_save_plots==1
  fprintf('Starting Saving
')
  set(gcf,'PaperUnits','inches','PaperPosition',[0 0 16 6]), print(f1,'-djpeg','-r600','Output_plot')

  file='Output_data.xlsx'; Sheet='Flow_data';
  xlswrite(file,t_flow',Sheet, 'A1');%Write the results to the excel file
  xlswrite(file,DBU_flow_rate',Sheet, 'B1');%Write the results to the excel file
  xlswrite(file,N_brush',Sheet, 'C1');%Write the results to the excel file
  xlswrite(file,DBU_flow_rate(1,1:500:end)',Sheet, 'D1');%Write the results to the excel file
  xlswrite(file,N_brush(1,1:500:end)',Sheet, 'E1');%Write the results to the excel file
  xlswrite(file,N_brush_syn_max',Sheet, 'F1');%Write the results to the excel file

if op_MW_plots==1
  set(gcf,'PaperUnits','inches','PaperPosition',[0 0 16 6]), print(f2,'-djpeg','-r600','Output_plot_MW')
  file='Output_data.xlsx'; Sheet='MW_data';
  xlswrite(file,t_flow',Sheet, 'A1');%Write the results to the excel file
  xlswrite(file,Lac_in_pot',Sheet, 'B1');%Write the results to the excel file
  xlswrite(file,BB_MW',Sheet, 'C1');%Write the results to the excel file
end
fprintf('done
')
end

function out=Root_finder_secant(a,b,v2,C_DBU,k_rop,f_nor,Tube_vol,N_brush,N_brush_syn_max,f_lac_o)

%% Secant method
% Note: this is a numerical rootfinding algorithm that can fail if the
% intial guess are poor. The solution is to either make differnt intial
% guess or use a different solver.

% Intial guesses
pp=a;
m=eq_flow(pp,v2,C_DBU,k_rop,f_nor,Tube_vol,N_brush,N_brush_syn_max,f_lac_o);
ppp=b;
m2=eq_flow(ppp,v2,C_DBU,k_rop,f_nor,Tube_vol,N_brush,N_brush_syn_max,f_lac_o);
X=10; % Intial error value
k=1; % Starting iteration counter
% Algorithm
while X>10^(-8)
  fprintf('
%3.f \t %1.10f',k,pp)
  p=pp-m*(pp-ppp)/(m-m2);
  m2=m;
m=eq_flow(p,v2,C_DBU,k_rop,f_nor,Tube_vol,N_brush,N_brush_syn_max,f_lac_o);
  X=abs(p-pp); % error calculation for stopping
  pp=p; %pp=p(n-1)
pp=p; % pp=p(n)
if k>50   % stopping criteria for max iterations
    fprintf('


!!!Max Iterations Reached!!!!!!!
')
    return
end
k=k+1;
end
if isnan(p)==1 || p<0
    fprintf('


!!!Secant method failed (suggest using higher DBU conc)!!!!!!!
')
    return
end
out=p;
end
function out=eq_flow(v1,v2,C_DBU,k_rop,f_nor,Tube_Vol,N_brush,N_brush_syn_max,f_lac_o)
% out=v1/(v1+v2)^3-1/(C_DBU*k_rop*f_nor*Tube_Vol)*log(1/(1-N_brush/N_brush_syn_max)); % First order monomer
pow=1.8;
out=v1/(v1+v2)^(2+pow)+((1-(1-N_brush/N_brush_syn_max)^(1-pow))*f_lac_o^(1-pow))/(C_DBU*k_rop*f_nor*Tube_Vol*(pow-1));
end
function out=Profile_fun_piecewise(x)   %%%% Change this for piecewise profile
if x<75
    out=75-x;
elseif x>75 && x<125
    out=75;
else
    out=x-125;
end
end

XIII. References


(5) Huggins, M. L. The Viscosity of Dilute Solutions of Long-Chain Molecules. IV.


