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14. ABSTRACT A new polymer architecture termed 'tapered bottlebrush' is proposed. Tapered bottlebrush polymers are derivatives of the traditional bottlebrush architecture, which consists of a backbone polymer with densely grafted side chain polymers. In the case of tapered bottlebrushes, the molecular weight of the side chain polymers will be systemically varied to yield anisotropic, cone-shaped nanostructures with side chain polymers that gradually increase in molecular weight along the length of the backbone polymer. This type of covalent, cone-shaped polymer may have applications in supercapacitor materials and as macromolecular, anisotropic amphiphiles.					
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Report Title

Final Report: Tapered Bottlebrush Polymers: A New Polymer Architecture (Topic 7.3 / 11.1)

ABSTRACT

A new polymer architecture termed 'tapered bottlebrush' is proposed. Tapered bottlebrush polymers are derivatives of the traditional bottlebrush architecture, which consists of a backbone polymer with densely grafted side chain polymers. In the case of tapered bottlebrushes, the molecular weight of the side chain polymers will be systemically varied to yield anisotropic, cone-shaped nanostructures with side chain polymers that gradually increase in molecular weight along the length of the backbone polymer. This type of covalent, cone-shaped polymer may have applications in supersoft elastomeric materials and as macromolecular, anisotropic amphiphiles. This submission deals predominantly with the synthesis of tapered bottlebrush polymers, which will be carried out using a dual polymerization approach based on ring-opening polymerization (ROP) and ring-opening metathesis polymerization (ROMP). The fast and living nature of both ROP and ROMP will allow for rapid production of the target polymers, with conversion from monomer to tapered bottlebrush expected to be complete within an hour. ROP and ROMP were chosen due to their orthogonal chemistry in order to limit any side reactions occurring as a result of the dual polymerization strategy.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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Number of Manuscripts:

Books

Received Book

TOTAL:

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TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Radzinski, Scott C.	1.00	
FTE Equivalent:	1.00	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Matson, John B.	0.79	
FTE Equivalent:	0.79	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

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Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

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Total Number:

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Sub Contractors (DD882)

Inventions (DD882)

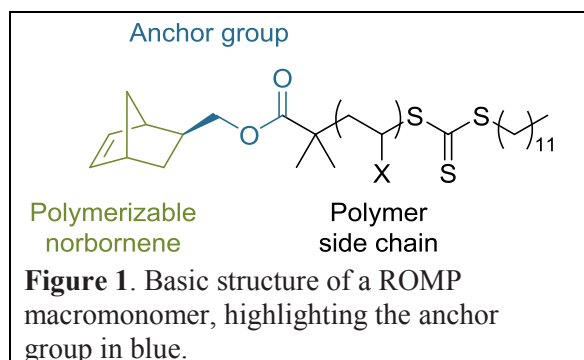
Scientific Progress

See attachment

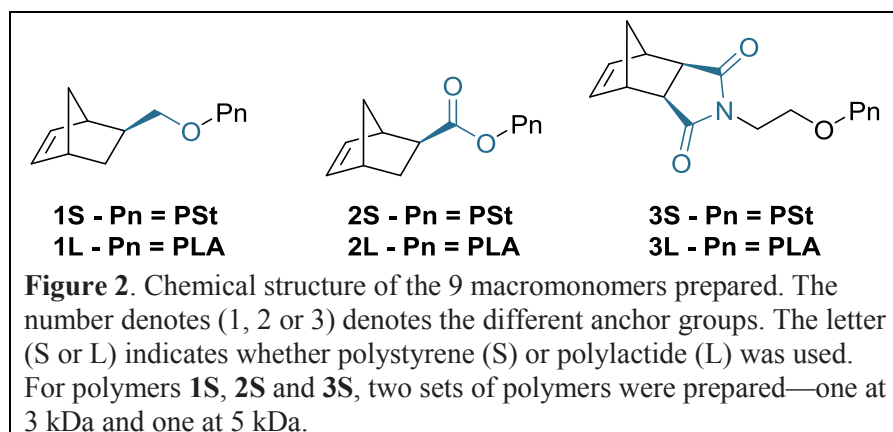
Technology Transfer

Scientific Progress and Accomplishments (description should include significant theoretical or experimental advances)

Successful synthesis of tapered bottlebrush polymers, as laid out in the proposal, requires achieving quantitative and rapid conversion using the grafting-through method of bottlebrush synthesis. Before attempting to prepare tapered bottlebrush polymers, we needed to understand what factors affected the efficiency (rate and ultimate conversion) of the grafting-through process using ring-opening metathesis polymerization (ROMP). We expected that the anchor group (Figure 1) would have a meaningful effect on the efficiency of the polymerization.



The anchor group connects the polymerizable norbornene to the polymer chain. The potential for chelation of the anchor group can affect both catalyst stability and lifetime. To this end, we prepared three sets of macromonomers, each with identical molecular weights but varied anchor groups (Figure 2).



Kinetics experiments were run on all nine macromonomers. The rate of polymerization must be as high as possible for the synthesis of precise tapered bottlebrush polymers. An example of the kinetics data obtained by measuring monomer conversion by NMR is shown in Figure 3. In this figure, three polymers with identical molecular weights (5000 Da) but varied anchor groups were evaluated. Similar data were obtained for the other two sets of polymers (PS-5000 and polylactide-3000). The data for all of the macromonomers are shown in Table 1. We are currently preparing a publication on this topic with collaborators who are simulating the proposed chelation interactions.

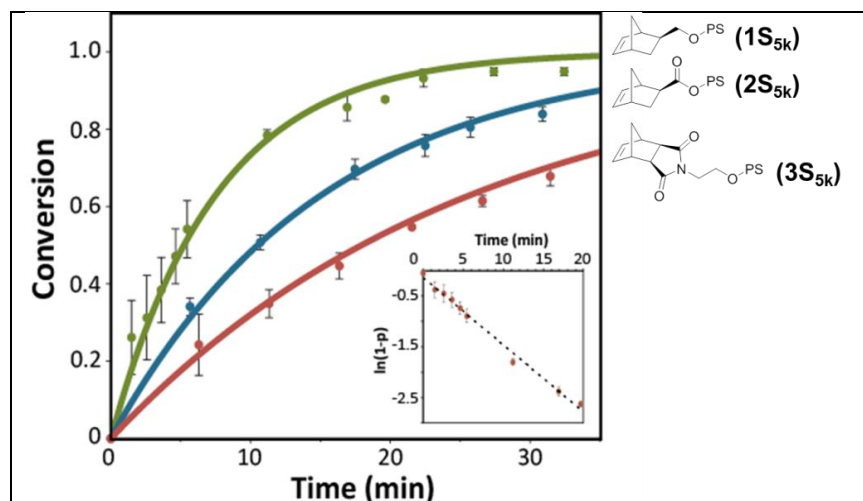


Figure 3. Kinetics study of polymers $1S_{5k}$, $2S_{5k}$ and $3S_{5k}$. We conclude that the lack of any chelation to the Ru metal center for polymers with anchor group **1** allow for faster polymerization.

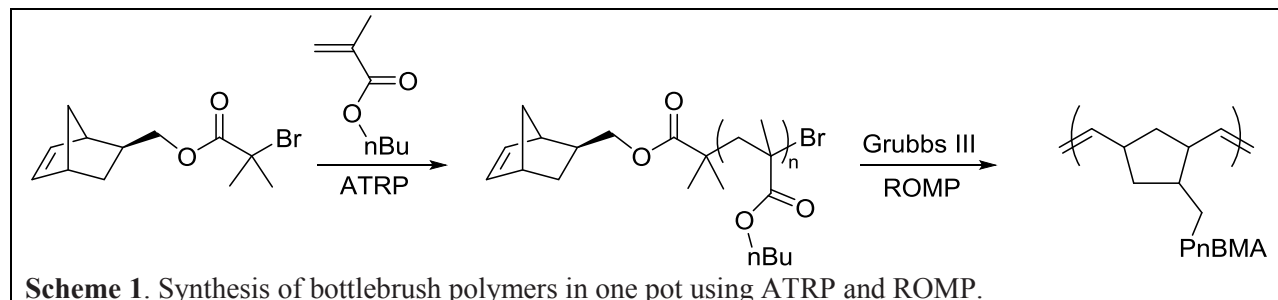
MM Name	k_p ($10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	$t_{1/2}$ (s)	k_{rel}
$1S_{3k}$	11 ± 2	68 ± 20	6.9
$2S_{3k}$	3.3 ± 0.3	210 ± 20	2.1
$3S_{3k}$	1.6 ± 0.2	450 ± 80	1
$1S_{5k}$	2.9 ± 0.4	250 ± 40	4.5
$2S_{5k}$	1.1 ± 0.1	620 ± 70	1.7
$3S_{5k}$	0.64 ± 0.07	1100 ± 100	1
$1L_{4k}$	8.1 ± 0.7	87 ± 9	4.8
$2L_{4k}$	5.1 ± 0.4	140 ± 10	3.0
$3L_{4k}$	1.7 ± 0.3	420 ± 70	1

Table 1. Kinetic data for all macromonomers. Relative rate constants (k_{rel}) are all relative to anchor group 3 for each set of macromonomers.

With the data in hand that anchor group 1 is best for the ROMP grafting-through component of the tapered bottlebrush synthesis, the next step was to determine a method for preparing conventional bottlebrush polymers in one-pot. We chose to pursue both atom-transfer radical polymerization (ATRP) ring-opening polymerization (ROP) as methods for making the arms along with ring-opening metathesis polymerization (ROMP) to generate the bottlebrush backbone. The results for each of these methods are described below.

ATRP-ROMP

ATRP and ROMP are theoretically orthogonal to each other. ATRP uses electron poor olefins (e.g., methacrylates) that do not participate in ROMP. In contrast, the best ROMP substrates are electron rich olefins (e.g., norbornene), which are typically not reactive towards radicals under ATRP conditions. Thus, we attempted a one-pot synthesis of bottlebrush polymers by combining ATRP and ROMP (Scheme 1).



In the first step, ATRP was carried out on n-butyl methacrylate (nBMA) from a norbornene-functionalized α -bromoester initiator. To reduce the amount of copper in solution, which might interfere with ROMP, we used SARA ATRP (SARA = supplemental activator and reducing agent), which uses CuBr_2 (50 ppm) and copper wire. This reaction typically worked well, yielding polymers with controllable molecular weights and low dispersities (\mathcal{D}) (Table 2, M_n MM and \mathcal{D} MM columns). ATRP reactions are typically stopped before full conversion, so remaining in the pot after quenching the ATRP reaction by removing the copper wire are excess nBMA monomer and copper(II)-ligand complex.

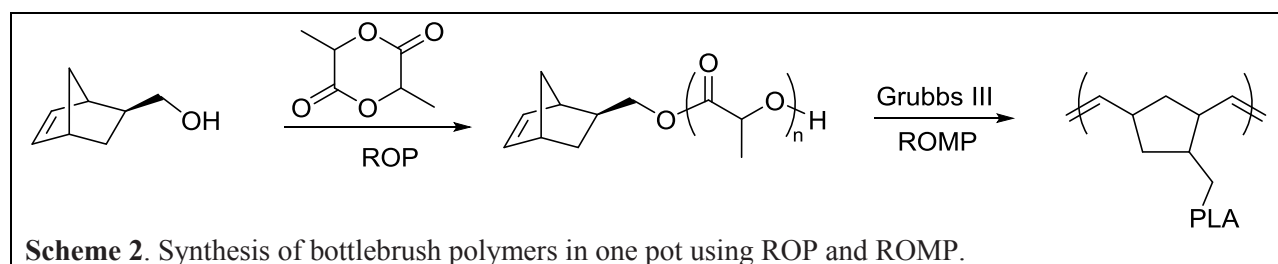
In the second step, Grubbs 3rd generation catalyst was added to effect ROMP. Conversion to bottlebrush was typically high (>89%). However, some control was lost as dispersity values increased to as high as 1.8 and theoretical M_n values did not match those measured by GPC. We attribute this loss of control to the copper-ligand complex, which appears to have a detrimental effect on ROMP. Efforts to address this problem are currently underway.

Entry	M_n MM	\mathcal{D} MM	BB M:I ratio	Conversion to BB	M_n BB (KDa)	Theo M_n (KDa)	\mathcal{D} BB
1	5200	1.11	25:1	89%	85	91	1.20
2	4600	1.05	50:1	92%	135	164	1.54
3	4300	1.17	100:1	94%	147	384	1.81

Table 2. Results for ATRP-ROMP one-pot bottlebrush studies.

ROP-ROMP

Although traditionally ROP has been carried out using a $\text{Sn}(\text{oct})$ catalyst, ROP can also be mediated by organic bases. To avoid deleterious reactions with the ruthenium catalyst as observed in the ATRP-ROMP case, we chose the organic base DBU as the catalyst for the ROP reaction of lactide (Scheme 2). The DBU was paired with benzoic acid to control the kinetics of the polymerization (Table 3, M_n MM and \mathcal{D} MM columns)



In the second step, trifluoroacetic acid (TFA) was added along with Grubbs 3rd generation catalyst. TFA was added to quench the ROP reaction and was chosen after screening several different types of acid additives. Most appeared to be too weak to fully scavenge the DBU, which can kill the ROMP catalyst.

Using TFA as a quencher, however, led to high bottlebrush conversions (> 80%). Observed molecular weights of the bottlebrush polymers matched those predicted based on macromonomer molecular weights and M:I ratios (Figure 4), and dispersities remained low for M:I ratios below 100.

BB M:I Ratio	M_n MM	\bar{D} MM	Conversion to BB	M_n BB (KDa)	Theo M_n (KDa)	\bar{D} BB
25	5800	1.01	87%	125	145	1.13
50	5900	1.01	84%	280	295	1.07
100	5700	1.01	82%	554	570	1.18
200	5600	1.02	80%	1034	1120	1.50

Table 3. Results for ROP-ROMP one-pot bottlebrush studies.

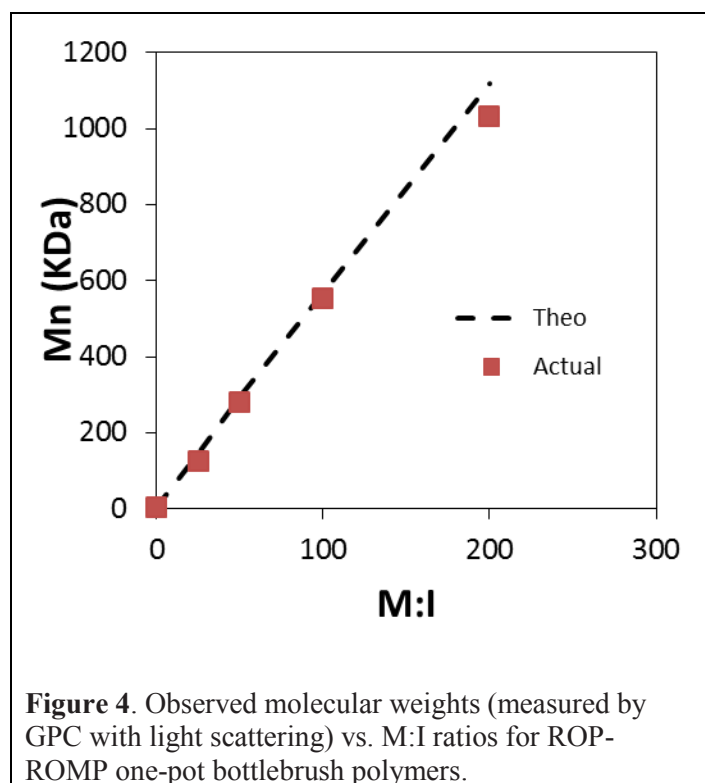


Figure 4. Observed molecular weights (measured by GPC with light scattering) vs. M:I ratios for ROP-ROMP one-pot bottlebrush polymers.

A publication is currently being drafted describing the ROP-ROMP one pot bottlebrush polymerization procedure, and efforts are underway to translate these results into tapered bottlebrush polymers using methods described in the original proposal.