

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 31-05-2011		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-Sep-2009 - 14-Sep-2010	
4. TITLE AND SUBTITLE Final Report: Advanced Nanomaterials from Functional Cyclic Polymers				5a. CONTRACT NUMBER W911NF-09-1-0512	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS Robert H. Grubbs, Andrew J. Boydston				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES California Institute of Technology Sponsored Research MC 201-15 California Institute of Technology Pasadena, CA 91125 -				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 56486-CH.1	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT The primary objective of this research program is to explore new possibilities for functional cyclic polymers in materials science. The exploration of new materials based upon cyclic polymer architectures has been stifled due to a general inability to produce cyclic polymers of high purity and controlled molecular weight on a large scale. During the funding period, we have significantly improved the synthetic capabilities toward cyclic polymers by developing catalyst and macromonomers amenable to direct formation of ultrahigh molecular weight cyclic brush					
15. SUBJECT TERMS Functional cyclic polymers					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Robert Grubbs
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 626-395-6003

Report Title

Final Report: Advanced Nanomaterials from Functional Cyclic Polymers

ABSTRACT

The primary objective of this research program is to explore new possibilities for functional cyclic polymers in materials science. The exploration of new materials based upon cyclic polymer architectures has been stifled due to a general inability to produce cyclic polymers of high purity and controlled molecular weight on a large scale. During the funding period, we have significantly improved the synthetic capabilities toward cyclic polymers by developing catalyst and macromonomers amenable to direct formation of ultrahigh molecular weight cyclic brush polymers. Additionally, to expand the scope of potential applications, we have prepared amphiphilic cyclic polymers in which each repeat unit bears complementary hydrophobic and hydrophilic side chains.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

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

“Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers” Xia, Y.; Boydston, A. J.; Grubbs, R. H. Angew. Chem. Int. Ed. 2011, 50, in press (DOI: 10.1002/anie.201101860).

Number of Papers published in peer-reviewed journals: 1.00

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

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

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

239th National Meeting of the American Chemical Society, San Francisco, CA, March 2010. Seminar Title: Recent Developments in Ring-Expansion Metathesis Polymerization. Andrew J. Boydston and Robert H. Grubbs.

239th National Meeting of the American Chemical Society, San Francisco, CA, March 2010. Seminar Title: Synthesis and Self-Assembly of Brush Polymers. Yan Xia and Robert H. Grubbs.

66th Southeast Regional Meeting of the American Chemical Society, New Orleans, LA, December 2010. Seminar Title: Synthesis of Cyclic Polymers via Ring-Expansion Metathesis Polymerization. Andrew J. Boydston and Robert H. Grubbs.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 3

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

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Matthew Van Wingerden	0.50
FTE Equivalent:	0.50
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>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Nebojsa Momcilovic	0.50
Anna Ivanova	0.50
Shuaili Li	0.50
Jason Lee	0.50
Shannon Mohler	0.50
Samuel Elder	0.50
FTE Equivalent:	3.00
Total Number:	6

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Progress Report

Project Title: Advanced Nanomaterials from Functional Cyclic Polymers
Award Number: W911NF-9-1-0512
Principal Investigator: Robert H. Grubbs, California Institute of Technology
Correspondent: Andrew J. Boydston, University of Washington
Award Period: 09/15/2009 – 09/14/2010

Summary of Research Accomplishments:

The first step toward developing complex cyclic brush polymers was to explore direct polymerization of norbornene-based macromonomers via ring-expansion metathesis polymerization (REMP). We found that macromonomers with molecular weights ranging from 2,200 to 8,700 Da were efficiently polymerized using our recently developed **SC-5** and **SC-6** catalysts; key data are summarized in Table 1. Polymer functionality including polystyrene, polylactide, and polyacrylate were each readily incorporated. Notably, the MWs of these cyclic brush polymers significantly exceeded those of the linear brush polymers we previously synthesized using ring-opening metathesis polymerization (ROMP).^{6d,12} The lack of analogous linear counterparts at similar MWs made it difficult to compare dilute solution properties between cyclic and linear brush polymers. Therefore, we primarily used imaging techniques to determine their topology.

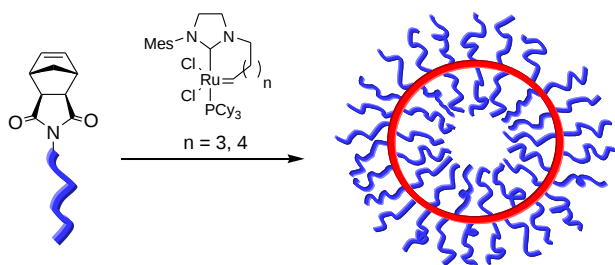


Table 1. REMP of Macromonomers.^[a]

Entry	Macromonomer ^[b]	catalyst	M_w ($\times 10^6$ Da) ^[c]	PDI ^[d]	DP _{backbone} ^[e]	Conversion ^[f]
1	NB(PS)2200	SC-5	9.1	1.2	4100	93%
2	NB(PS)3200	SC-5	6.2	1.1	1900	74%
3	NB(PS)6600	SC-5	5.8	1.1	880	67%
4 ^g	NB(PS)6600	SC-5	5.7	1.2	860	55%
5	NB(PLA)4400	SC-5	13	1.4	3000	92%
6	NB(PLA)8700	SC-5	26	1.1	3000	79%
7	NB(PS)2200	SC-6	2.4	1.2	1100	89%
8	NB(PS)6600	SC-6	6.5	1.1	1000	78%
9	NB(PnBA)4000	SC-6	4.0	1.3	1000	>99%
10	NB(PLA)4400	SC-6	1.9	1.5	430	>99%
11	NB(PLA)8700	SC-6	6.0	1.4	690	98%

[a] Conditions: [MM/catalyst]=50, 55 °C, in benzene unless otherwise noted. [b] MMs were named in a format of NB(X)Y, with X the type of polymer and Y the M_n of MM. [c] Determined by multi-angle laser light scattering. [d] Determined by GPC in THF. PDI is likely underestimated due to the ultrahigh MWs that exceed the GPC column size exclusion limit. [e] DP of brush polymer. [f] Conversion of MM is determined by comparing the peak areas of brush polymer and residual MM from GPC measurement of the crude product. [g] THF was used as solvent.

As shown in Figure 1, various large ring-shaped nanostructures were clearly observed, either as small aggregates or as individual rings, together with some linear chains. Each of the observed nanostructures, both cyclic and linear, had uniform width of 30-40 nm and height of 1-2 nm, which are consistent with the linear brush polymer we previously prepared via ROMP of the same MMs. Most cyclic structures have diameters in the range of 100-180 nm, corresponding to contour lengths of 310-560 nm. We have previously measured the length per monomeric unit to be 0.62 nm,¹² using uniform, narrowly dispersed linear brush polymers with the same side chain. Therefore, a contour length of 310-560 nm corresponds to a backbone DP of ca. 500-900,

which is close to the calculated backbone DP (880) based on the absolute MW measured by light scattering. Additionally, each cyclic structure exhibited loop-like shapes with large open pores, different from our previously reported cyclic dendronized polymers that presented as donut-like shapes with small pores of only 5-7 nm.¹¹ This is presumably due to the high MWs of both side chain and backbone and significantly extended backbone conformation with very high grafting density (1 side chain per repeat unit) in these polymers. Interestingly, we also observed structures where cyclic loops either partially stacked or crossed (Figure 1e), and the cross-sectional analysis showed that the stacked portion has a height twice that of the non-overlapping portion. We believe this structure is more likely to be from physically, partially overlapped rings during spin-coating and drying process, as opposed to catenated rings. Formation of catenanes during metathesis polymerization of norbornenyl macromonomers is very unlikely because chain transfer between greatly hindered polynorbornene backbones should not be possible.

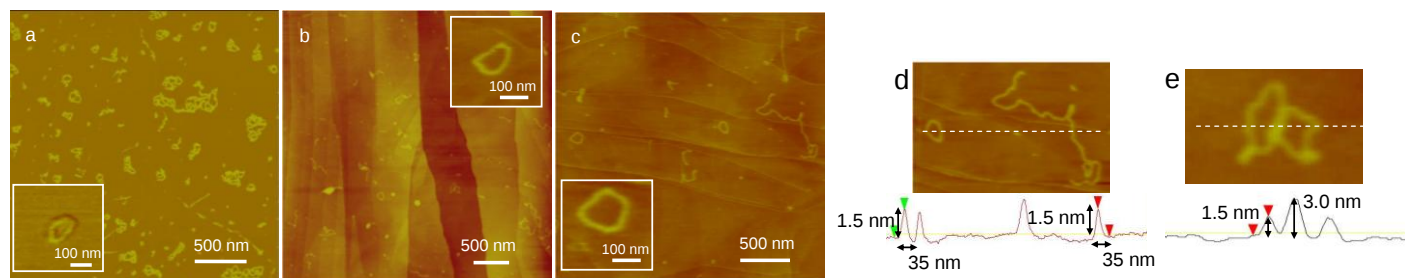


Figure 1. Topographic AFM images of REMP brush polymer **PNB-g-PS6600** (Table 1, entry 3) on graphite: (a) spin coated from 0.01 mg/mL solution; (b-c) spin coated from 0.001 mg/mL solution. Insets are magnified images of individual cyclic brush polymers; (d) cross-sectional analysis of a cyclic and a linear brush polymer; (e) cross-sectional analysis of either stacked or crossed rings.

With the successful REMP of hydrophobic macromonomers described above, we next targeted more complex amphiphilic systems comprising both hydrophilic and hydrophobic chains on each macromonomer (Figure 2). Starting from carbic anhydride (**1**), esterification with 10-undecyne-1-ol provided “clickable” alkyne in good yield. Subsequent PEG (550 Da) attachment gave diester **3**, and azide-alkyne “click” chemistry was used to install the hydrophobic polystyrene (2,200 Da) side chain yielding amphiphilic macromonomer **4** in 72% overall yield. Treatment of **4** with our most active REMP catalyst (**SC-6**) provided cyclic polymer **5**, though in low 34% isolated yield. Analysis via gel-permeation chromatography (GPC) revealed an M_w of 1.5 MDa, but a non-uniform (i.e., multimodal) molecular weight distribution was observed. Attempts to gain control over the molecular weight, and also to access lower molecular weight ranges involved addition of Ph_3P to the polymerization. While this yielded polymers down to 500 kDa, and with monomodal GPC traces, polymerization times were greatly extended and catalyst decomposition resulted in low yields of isolable polymer. Current efforts focus on improving the polymerization efficiency through new catalysts designs, as well as characterization of the amphiphilic cyclic polymers that have been produced.

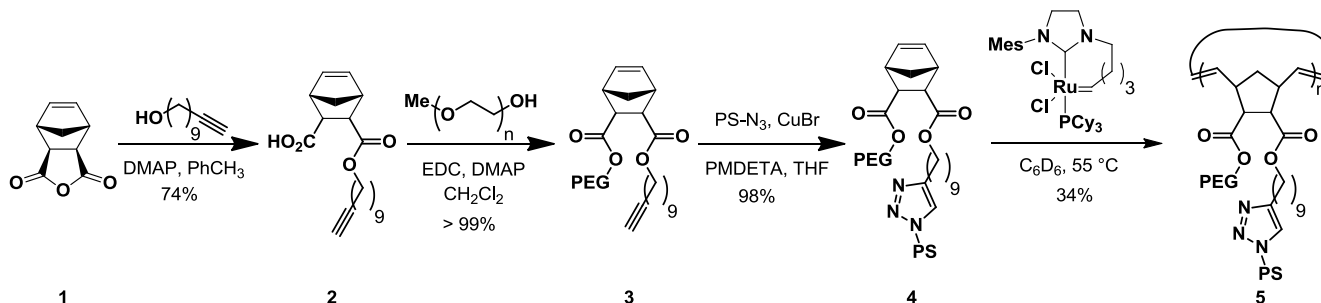


Figure 2. Synthesis of amphiphilic macromonomer and REMP to give an amphiphilic cyclic polymer.

Papers Published in Peer-Reviewed Journals (total = 1)

“Synthesis and Direct Imaging of Ultrahigh Molecular Weight Cyclic Brush Polymers” Xia, Y.; Boydston, A. J.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2011**, 50, in press (DOI: 10.1002/anie.201101860).

Presentations (total = 3)

239th National Meeting of the American Chemical Society, San Francisco, CA, March 2010. Seminar Title: Recent Developments in Ring-Expansion Metathesis Polymerization. Andrew J. Boydston and Robert H. Grubbs.

239th National Meeting of the American Chemical Society, San Francisco, CA, March 2010. Seminar Title: Synthesis and Self-Assembly of Brush Polymers. Yan Xia and Robert H. Grubbs.

66th Southeast Regional Meeting of the American Chemical Society, New Orleans, LA, December 2010. Seminar Title: Synthesis of Cyclic Polymers via Ring-Expansion Metathesis Polymerization. Andrew J. Boydston and Robert H. Grubbs.

Students Supported

Anna Ivanova	(undergraduate, hourly wages, 50% FTE)	\$1,141.23
Shuaili Li	(undergraduate, SURF program, 50% FTE)	\$3,000.00
Samuel Elder	(undergraduate, SURF program, 50% FTE)	\$3,000.00
Jason Lee	(undergraduate, SURF program, 50% FTE)	\$6,000.00
Shannon Mohler	(undergraduate, hourly wages, 50% FTE)	\$820.50
Nebojsa Momcilovic	(undergraduate, hourly wages, 50% FTE)	\$5,064.00

Matthew Van Wingerden	(graduate student, 50% FTE)	\$1,687.50
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Total Salaries and Wages: \$20,713.23