RICE UNIVERSITY

Structure and Function of Bottlebrush Polymers

by

Stacy Lee Pesek

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Rafael Verduzco, Louis Owen Assistant Professor, Chemical and Biomolecular Engineering

Walter Chapman, William W Akers Professor, Chemical and Biomolecular Engineering
Associate Dean for Energy, George R. Brown School of Engineering

Christy Landes, Associate Professor of Chemistry and Electrical and Computer Engineering

Houston, Texas
December 2015
This thesis is dedicated to my beloved grandfather Johnny Atwood, whose engineering career, strong will, and intelligence inspired me to pursue engineering. We miss you dearly.
Acknowledgements

I would like to express my appreciation to my advisor Dr. Rafael Verduzco for teaching me to push the limits of polymer science with an ever-positive perspective on what can be achieved. Thank you for finding a way for me to join your lab, for encouraging me to attend multiple national and local conferences and guiding me to find my own contributions to the polymer community.

I would also like to thank Walter Chapman, Christy Landes and Mauro Ferarri for serving on my thesis committee. I would like to extend my gratitude to Dr. Walter Chapman for being a personal mentor that I could turn to anytime throughout my five years at Rice. Your caring attitude towards all students has made a lasting impression. I would like to thank Christy Landes for your willingness to serve on my committee and for providing thought-provoking questions. I would also like to thank Mauro Ferarri for taking time to serve on my committee and provide a practical perspective on polymers for drug delivery. Thank you for your thoughtful discussions and encouragement to pursue my research.

During my doctoral research, I also had a tremendous amount of help from collaborators. I would like to thank Dr. Boualem Hammouda at the National Institute of Standards and Technology, Center for Neutron Research for numerous insightful conversations about polymers and neutron interactions, for helping me operate the neutron beam-line and, importantly, how to formulate proper experiments with limited time. Thank you for your wisdom, guidance and willingness to help me. I would also like to thank Dr. Gila Stein at the University of Houston for your help with my more recent projects relating bottlebrush polymers films. Thank you for providing assistance with thin films and your help revising manuscripts. Thank you Adeline Mah (graduate student in Dr. Steins lab) for your friendly smile and willingness to learn from my synthesis experience.

I would like to acknowledge my friends and colleagues, Dr. Xianyu Li, Dr. Aditya Agrawal, Dr. Kendall Smith and Dr. Yen Hao Lin for all the discussions in the office, shared meals at conferences, and for guiding the way through a polymer doctoral degree.
To my more recent labmates Luqing Qi, Jorge Wu Mok, Bohan Zhu, Xiayoi Li, and Zhiqi Hu, thank you for your kindness and especially for helping me with various tasks while I was pregnant during my research. I wish you the best of luck in your continued studies. I would especially like to thank the five undergraduate students I had the extreme privilege of mentoring over the past five years, Sarah Southmayd, Qianhong Zhu, Qiqi Zhang, Will Kasper and Ryan Reynolds. Thank you for your contributions to my research, trusting me to lead you, and for the energy you brought to the lab. I am truly grateful for the experience I had with each of you.

To the National Science Foundation, thank you for honoring me with the graduate research fellowship, which funded three years of my doctoral research at Rice. Thank you for continuously supporting young scientists with financial backing that allows us to pursue what we find interesting and exciting, rather than only what has existing funding. I would also like to thank the Chemical and Biomolecular Engineering Department at Rice for accepting me into the doctoral program and for the early support in my degree.

I would like to sincerely thank my friends and family who have helped me reach my educational goals. To my mom Karen, thank you for your unconditional love and support throughout my childhood and many, many years of educational formation. To my dad Andrew, thank you for teaching me and my brother the value of hard work from a young age and for passing on a love of science. Jon, thank you for tolerating me as your big sister and for challenging my math skills daily while we were growing up. David and Debbie, thank you for your love and support over the years. I would also like to thank Dr. Joann Pearson, my friend and cousin, for all the coffee, conversations, and laughs throughout the last nine years of our academic studies. To my parents-in-law, Larry and Charlene Pesek, thank you for your love and support of my pursuit of my doctorate degree. Larry, I truly appreciated being able to talk about polymers with you. Thank you Francesca Mirri for being a wonderful friend and roommate, for sharing my love of cooking, and for being such a great friend and someone I could complain to (and with) about all the challenges and hard times of graduate school.

Last, and most of all, I would like to thank my wonderful, loving and supportive husband Keith. You believed in me when I didn’t believe in myself and motivated me to work
hard when I wanted to slack off. Thank you for being my foundation. I could not have done this without you. And to my precious daughter Madelyn, thank you for granting me with the humbling task of being your mother. Without knowing it, your life grounded me and gave me the final motivation I needed to complete my research. I thank God every day for the blessings of my husband and daughter.
Abstract

Bottlebrush polymers, also known as molecular brushes, are a special class of polymers characterized by having a “side-chain” polymer grafted to every repeating unit along the main chain polymer “backbone”. This high grafting density is the source of unique and interesting physical properties, many of which are still actively being studied. The physical size and structure of bottlebrush polymers is governed by the length (degree of polymerization, $DP$, or molecular weight, $M_n$) of the side-chain and backbone polymers. The chemical properties (such as solubility, responsive behavior, etc) are governed primarily by side-chain polymer type or monomer selection. Together, the side-chain and backbone polymers determine bottlebrush molecular structure properties such as size, shape and stiffness. The type of side-chain polymer dictates bottlebrush functional properties, such as interaction with environment, hydrophobicity, and self-assembled structures.

The main objective of the work described in this thesis is to develop an improved understanding of the relationship between bottlebrush structures and resulting material properties such that bottlebrush materials can be tailored to meet functional needs for target applications. These applications include drug delivery, where the size and shape of the bottlebrush in solution are important and as thin film coatings, where the side-chain structure and flexibility determines surface properties. The first chapter introduces bottlebrush polymers and discusses their synthesis and physical properties.

The second chapter describes a study of the solution conformation of a series of bottlebrush polymers with polystyrene side-chains. The structure of the bottlebrushes was changed by varying the side-chain and backbone polymer lengths ($M_n$), which was quantified by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and light scattering analysis. Solution conformation of bottlebrush polymers in toluene (a good solvent for polystyrene side-chains) was determined by fitting theoretical models to experimental small-angle neutron scattering (SANS) data. In this first study we
measured a conformation change from globular molecules to highly elongated cylinders when bottlebrush backbones exceed 100 repeat units.

Chapter three details a similar SANS study on bottlebrush polymers with biocompatible poly(lactic acid) (PLA) side-chains. Well-defined PLA bottlebrushes with two side-chain lengths and systematic variations in backbone length were made, resulting in a total of nine bottlebrush samples. The samples display a similar change in conformation from globular to elongated after the backbone length exceeds 50 units for both side-chain lengths. Bottlebrush radii were dependent primarily on side-chain length, and bottlebrush length increases with backbone size, as expected. By fitting the results for bottlebrush radii with a power-law model, we found side-chain polymer conformation scales with length as $\nu = 0.56 \pm 0.013$, consistent with a 3-dimensional self-avoiding walk.

Next, we studied bottlebrush polymers as additives to thin films that spontaneously migrate to the top film surface, allowing small amounts of polymer to significantly change the surface properties in polymer coatings. Novel poly(dimethyl siloxane) (PDMS)-based bottlebrush polymers and PDMS-PLA bottlebrush copolymers were synthesized and cast in films as additives. Surface properties of bulk polymer and polymer with 1 or 5 wt % bottlebrush copolymer additives were characterized by contact angle, X-ray photoelectron spectroscopy (XPS) and microscopy. Mixed-arm PDMS/PLA bottlebrush copolymers spontaneously segregate to the top interface with large surface excess, which result in changes in water contact angle of over 30 ° in some cases. In most cases, these bottlebrush polymers did not induce phase separation in thin films. Bottlebrush polymer segregation in thin films is attributed to both entropic demixing of branched species from a linear matrix and enthalpic migration to the polymer-air interface with a low-surface energy polymer (PDMS).

In the fifth chapter we present bottlebrush copolymers with poly(ethylene glycol) (PEG) and PLA components with hydrophobic cores for drug encapsulation and release applications. Bottlebrush copolymers were synthesized with “core-shell” architecture from PLA-PEGA linear side-chains resulting in a hydrophobic core and hydrophilic, water soluble shell. A second type of bottlebrush copolymers, “blocky” bottlebrushes, was synthesized with a block copolymer backbone from PLA and PEG homopolymer
side-chains. These “blocky” bottlebrushes self-assemble in water to form large, spherical micelle structures. Bottlebrush copolymers were characterized by SANS, dynamic light scattering (DLS), and electron microscopy to determine size and shape of bottlebrush materials.

An outlook on future applications of bottlebrush polymers and preliminary data is presented in chapter six. Small amounts of nanoparticle additives have been shown to have significant changes in composite thermal properties. Using a hypothesis presented in recent literature, we calculate the surface free energies of bottlebrush polymers and linear host polymers (PS and poly(methyl methacrylate) (PMMA)) and predict a directional change in host glass transition temperature. Bottlebrush polymer additives in bulk polymers are prepared from 1 – 40 wt % additives and composite glass transition temperature is measured by differential scanning calorimetry (DSC). Bottlebrush polymers could also be beneficial as surface coatings for anti-biofouling applications. Brush polymers and thermoresponsive materials, such as poly(N-isopropyl acrylamide) (PNIPAAm) have demonstrated decreased adhesion from fouling biomass. We discuss the synthesis of crosslinkable PNIPAAm bottlebrush polymers and the preparation of thin film coatings to be studied for anti-biofouling.
# TABLE OF CONTENTS

DEDICATION .................................................................................................................. I

ACKNOWLEDGEMENTS .................................................................................................. II

ABSTRACT ...................................................................................................................... V

1. INTRODUCTION .......................................................................................................... 1

   1.1 Bottlebrush Polymer Structure .............................................................................. 1
   1.1.1 Bottlebrush Polymer Synthesis ........................................................................... 3
   1.1.2 Bottlebrush copolymers ...................................................................................... 7
   1.2 Functional Applications of Bottlebrush Polymers ................................................... 8
   1.3 REFERENCES ......................................................................................................... 12

2. SMALL ANGLE NEUTRON SCATTERING ANALYSIS OF BOTTLEBRUSH POLYMERS
   MADE BY GRAFTING THROUGH .................................................................. 18

   2.1 ABSTRACT ............................................................................................................. 18
   2.2 INTRODUCTION .................................................................................................... 19
   2.3 EXPERIMENTAL ................................................................................................... 21
      2.3.1 Materials ....................................................................................................... 21
      2.3.2 Instrumentation ............................................................................................. 23
   2.4 RESULTS ................................................................................................................ 24
      2.4.1 Bottlebrush Polymer Synthesis ....................................................................... 24
      2.4.2 SANS Measurements and Analysis ............................................................... 27
      2.4.3 TEM Analysis .................................................................................................. 36
   2.5 DISCUSSION .......................................................................................................... 37
   2.6 REFERENCES ......................................................................................................... 40

3. STRUCTURAL PROPERTIES OF POLY(NORBORNE)-GRAFTED-POLY(LACTIC ACID)
   BOTTLEBRUSH POLYMERS DETERMINED BY SANS ..................................... 44

   3.1 INTRODUCTION .................................................................................................... 46
   3.2 RESULTS AND DISCUSSION ................................................................................. 43
      3.2.1 PNB-g-PLA Bottlebrush Synthesis .................................................................. 46
      3.2.2 SANS .............................................................................................................. 48
      3.2.3 Size Analysis by TEM and DLS ...................................................................... 55
      3.2.4 Bottlebrush Thermal Properties ..................................................................... 58
   3.3 CONCLUSION ......................................................................................................... 59
   3.4 EXPERIMENTAL .................................................................................................... 60
      3.3.1 Materials ....................................................................................................... 60
      3.3.2 Instrumentation ............................................................................................. 61
   3.5 REFERENCES ......................................................................................................... 62

4. PDMS-BASED BOTTLEBRUSH COPOLYMERS FOR SURFACE ACTIVE ADDITIVES.....66

   4.1 ABSTRACT ............................................................................................................. 66
   4.2 INTRODUCTION .................................................................................................... 67
   4.3 EXPERIMENTAL .................................................................................................... 71
      4.3.1 Materials ....................................................................................................... 71
      4.3.2 Instrumentation ............................................................................................. 75
LIST OF FIGURES

Figure 1.1 Schematic of bottlebrush polymer ................................................................. 2
Figure 1.2 Images of bottlebrushes on a surface ............................................................. 3
Figure 1.3 Synthetic approaches of bottlebrush polymers ................................................. 4
Figure 1.4 Controlled synthesis by grafting-through macromonomers .............................. 5
Figure 1.5 RAFT mechanism ............................................................................................ 6
Figure 1.6 Chemical structure of norbornene-functionalized CTA .................................... 7
Figure 1.7 Structures of bottlebrush copolymers .............................................................. 8
Figure 1.8 Blocky and mixed-arm bottlebrush polymers .................................................. 9
Figure 1.9 Examples of biocompatible bottlebrush polymers Synthesis .......................... 11
Figure 1.10 Cryo-TEM images of self-assembled polymers and in-vivo studies ............ 12

Figure 2.1 Schematic for a bottlebrush polymer ............................................................... 20
Figure 2.2 1H NMR spectra of polystyrene bottlebrush .................................................. 22
Figure 2.3 SANS scattering intensity polymers ............................................................... 27
Figure 2.4 SANS data and Guinier-Porod and cylinder model fits .................................. 28
Figure 2.5 Results and analysis by the Guinier-Porod model ........................................ 31
Figure 2.6 Results from cylinder and flexible-cylinder models ....................................... 34
Figure 2.7 SANS as a function of temperature for PS bottlebrushes ............................... 35
Figure 2.8 Normalized length and dimension parameter for bottlebrush polymers ......... 36
Figure 2.9 TEM micrographs of select PS bottlebrush polymers ..................................... 37
Figure 2.10 Proposed structure for bottlebrush polymers ............................................... 38

Figure 3.1 GPC traces of PNB-g-PLA34 and PNB-g-PLA57 series .................................. 48
Figure 3.2 SANS traces for PLA bottlebrush series in 1,4-dioxane-d8 ............................ 49
Figure 3.3 SANS traces for PNB-g-PLA (Nc = 34) bottlebrush series in toluene-d8 ....... 50
Figure 3.4 Results from the Guinier-Porod and Flexible Cylinder models ...................... 53
Figure 3.5 TEM micrographs of bottlebrush polymers with PLA side-chains ............... 56
Figure 3.6 DLS number distributions for bottlebrush polymers (NBB = 57) in THF .......... 57
Figure 3.7 Glass transition temperature of PNB-g-PLA determined by DSC. ............... 59

Figure 4.1 Schematic of bottlebrush polymer blends with linear polymer ..................... 68
Figure 4.2 Concentration of bottlebrush polymer (φ) as a function of depth into the film. 69
Figure 4.3 Modification of polymer thin films by addition of bottlebrush copolymers .... 70
Figure 4.4 GPC traces of PDMSX-NB macromonomers and P(PDMS-X)n bottlebrushes .... 79
Figure 4.5 GPC traces for PDMS/PLA bottlebrush copolymers .................................... 81
Figure 4.6 Water contact angle of films with 1 or 5 wt % bottlebrush copolymers .......... 83
Figure 4.7 Optical micrographs of films cast with 5 wt% bottlebrush copolymer .......... 85
Figure 4.8 XPS survey data for bottlebrush copolymer sample P(75PDMS-co-25PLA)100 .... 91
Figure 4.9 AFM images of bottlebrush copolymer blend films ..................................... 93

Figure 5.1 GPC traces of NB-PLA-b-PEG and “core-shell” bottlebrush polymers .......... 121
Figure 5.2 GPC traces of NB-PLA58-PEG5k copolymer and PNB(PLA58-PEG5k) .......... 122
Figure 5.3 Synthesis of blocky PLA-PEG bottlebrush polymers .................................. 123
Figure 5.4 ROMP kinetics of NB-PLA and NB-PEG homopolymer macromonomers .... 124
Figure 5.5 GPC traces during ROMP polymerization of “blocky” bottlebrush polymer .... 126
Figure 5.6 Dynamic light scattering size distributions of blocky bottlebrushes .......... 127
Figure 5.7 SANS scatter profiles for core-shell bottlebrush polymers ................................128
Figure 5.8 SANS and TEM blocky bottlebrush polymers .......................................................131

Figure 6.4 Preparation of PNb(NIPAAm-c-ABP) bottlebrush polymers ................................151
Figure 6.5 Chemical structure of fluorescent, water soluble NbP(NIPAAm-c-FMA) ........153
Figure 6.6 Fluorescent bottlebrush polymer dry and in water in white and UV light ..........141
LIST OF SUPPORTING FIGURES

Figure S4. $^1$H NMR spectroscopy for PDMS2k-NH$_2$ and PDMS2k-NB ........................................101
Figure S4.2 $^1$H NMR spectroscopy for PDMS5k-SiH, PDMS5k-NH$_2$ and PDMS5k-NB ..........102
Figure S4.3 DSC thermographs of PDMS2k bottlebrush polymers ........................................103
Figure S4.4 DSC thermographs of PDMS5k bottlebrush polymers ........................................104
Figure S4.5 DSC thermographs of bottlebrush copolymers P(XPDMS-co-YPLA)$_{100}$ ..............105
Figure S4.6 Polarized Optical microscopy images of bottlebrush copolymer films .................105
Figure S4.7 Optical micrographs of blends from 1% PDMS and linear diblock ......................106
Figure S4.8 Optical micrographs of blends from 5% PDMS and linear diblock .....................107
Figure S4.9 AFM height images for 1 wt % bottlebrush copolymer films ..............................107
Figure S4.10 AFM height images for 5 wt % bottlebrush copolymer films .............................108
Figure S4.11 AFM for pure PLA and P(75PDMS-co-25PLA)$_{100}$ showing similar “holes” .......108
Figure S4.12 Microscopy analysis of films, before and after thermal annealing .......................109
Figure S4.13 Tapping mode height and phase images for 1% P(75PDMS-co-25PLA)$_{100}$ .........110
Figure S4.14 SAXS data for as-cast P(50PDMS-co-50PLA)$_{100}$ showing ordered features ....112
Figure S4.15 SAXS data for mixed arm bottlebrushes .........................................................113
Figure S4.16 Temperature dependent SAXS data for P(50PDMS-co-50PLA)$_{100}$ .....................114
Figure S4.17 SAXS data from P(PDMS2k-block-PLA$_{2k}$) ...............................................115
Figure S4.18 SAXS data from P(PDMS5k-block-PLA$_{5k}$) ................................................115
# LIST OF TABLES

**Table 2.1:** Properties of PS bottlebrush polymers PN(PSn)M ................................................................. 25  
**Table 2.2:** Reaction conditions for RAFT-based polystyrene macromonomer synthesis .......... 26  
**Table 2.3:** Results from Guinier-Porod model ......................................................................................... 30  
**Table 2.4:** Results from rigid cylinder and flexible cylinder models ......................................................... 33

**Table 3.1:** Properties of PNb−g−PLA bottlebrush polymers with Nsc = 34 and 57 .................. 47  
**Table 3.2:** Fitted results for Guinier-Porod model of PNb-g-PLA bottlebrush SANS ............ 51  
**Table 3.3:** Fitted results for cylinder and flexible cylinder models ......................................................... 54  
**Table 3.4:** Chain extension analysis for PNb-g- in 1,4 dioxane-d8 ......................................................... 55  
**Table 3.5:** Summary of PNb-g-PLA thermal properties and size estimates ......................... 58

**Table 4.1** Chemical and thermal properties of PDMS bottlebrush polymers P(PDMS-X)n ....... 78  
**Table 4.2** Summary of thermal properties of PDMS bottlebrush polymers .......................... 80  
**Table 4.3** Properties bottlebrush copolymers with PDMS and PLA size-chains ...................... 82  
**Table 4.4** Contact angle results for blends cast with linear diblock additives ....................... 88  
**Table 4.5** Elemental composition of thin films determined by XPS measurements .............. 90  
**Table S4.1** Properties of PDMS-b-PLA linear diblock polymers ..................................................... 106

**Table 5.1:** Properties of NB-PLA-b-PEG and “core-shell” bottlebrushes ............................. 119  
**Table 5.2** Properties of “blocky” bottlebrush ............................................................................... 125  
**Table 5.3** Fitted results for core-shell bottlebrush polymer SANS data ................................. 125  
**Table 5.3** Fitted results for SANS data from blocky bottlebrush polymers ......................... 132
LIST OF EQUATIONS

EQN 2.1 GUINIER-POROD MODEL $Q < Q_1$ .................................................................................................. 29
EQN 2.2 GUINIER-POROD MODEL $Q > Q_1$ .................................................................................................. 29
EQN 2.3 GUINIER-POROD MODEL: DEFINITION OF D VARIABLE .............................................................. 29
EQN 2.4 GUINIER-POROD MODEL: DEFINITION OF $Q_1$ ............................................................................ 29
EQN 2.5 CYLINDER MODEL $P(Q)$ .............................................................................................................. 31
EQN 2.6 CYLINDER MODEL $F(Q, \alpha)$ ..................................................................................................... 32
EQN 2.7 FLEXIBLE CYLINDER MODEL $S(Q)$ ............................................................................................ 32

EQN 3.1 POLYMER RADIUS ........................................................................................................................ 54
EQN 3.2 POLYMER LENGTH ........................................................................................................................ 54

EQN 6.1 RELATIONSHIP BETWEEN CONTACT ANGLE AND SURFACE ENERGY ...................................... 141
LIST OF SCHEMES

SCHEME 2.1 SYNTHESIS OF POLYSTYRENE BOTTLEBRUSH POLYMERS.........................................................21

SCHEME 3.1 TWO-STEP SYNTHESIS OF Nb-PLAM MACROMONOMERS AND BOTTLEBRUSH .................46

SCHEME 4.1 SYNTHESIS OF PDMS BOTTLEBRUSH POLYMERS P(PDMS-X)$_n$.................................................77
SCHEME 4.2 SYNTHESIS OF BOTTLEBRUSH COPOLYMERS P(XPDMS-CO-YPLA)$_n$.................................81

SCHEME 5.1 SYNTHESIS OF NB-PLA-b-PEG AND P(NB-PLA-b-PEG)$_n$ BOTTLEBRUSH .......................120
1. Introduction

Polymer systems provide versatile materials for tailored nanoscale features in numerous applications. Typically polymer characteristics are tuned by varying the monomer (polymer type) and length (molecular weight), but more recently variations in polymer architecture are proving to result in interesting physical properties. Bottlebrush polymers are a special type of polymer architecture with densely packed side-chains grafted to a main chain polymer backbone. By controlling the length of the side-chains and backbone, bottlebrush polymers can range in size from tens of nanometers to several hundreds of nanometers and they can be cylindrical or spherical in shape. Variations in bottlebrush polymer features can include copolymer side-chains or mixed arm bottlebrush polymers. With modern polymer synthesis techniques the side-chain length, side-chain polymer type, backbone length, side-chain grafting density, and distribution of side-chains along the backbone can be tailored to accommodate specialized applications of bottlebrush polymers.

1.1 Bottlebrush Polymer Structure

Bottlebrush, or molecular brush, polymers are a unique branched polymer architecture in which every repeat unit along the main chain “backbone” polymer is covalently attached to a side-chain polymer (Figure 1.1). Ideally the grafting density (or percentage of backbone repeat units with a side-chain) is 100%. The tight packing of side-chains creates molecular frustration and steric repulsion. Crowding may force the backbone polymer to stretch significantly more than the linear equivalent. The side-chains will find the most thermodynamically favorable conformation (i.e. most evenly spaced) and thus assume a cylindrical morphology. The large cylindrical shape may be advantageous to many applications including surface modification \(^1,2\), drug delivery\(^3\), and anti-fouling\(^2,4,5\).
Figure 1.1 Schematic of bottlebrush polymer. The main polymer “backbone” is shown with grafted “side-chains” extending radially from the backbone [Pesek, *Macromolecules*, 2013].

The large macromolecular size of bottlebrush polymers allows direct visualization of single polymers by atomic force microscopy (AFM), scanning force microscopy (SFM) and transmission electron microscopy (TEM). This has led to a number of fascinatingly detailed images of individual bottlebrushes. Molecular brush backbone conformation can be directly visualized as a semi-flexible rod by AFM and SFM, as seen in Figure 1.2. In some cases even the side-chain polymers have been observed, confirming the highly stretched conformation when bottlebrush is dried on a flat surface. The conformation of bottlebrush polymers in solution cannot be directly visualized but studies on bottlebrush polymers in solution have been performed primarily by utilizing scattering techniques. The conformation of bottlebrush polymers in dilute solutions has been experimentally investigated by small angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and light scattering. These studies aim to resolve the macromolecular properties of bottlebrushes such as diameter, length, and stiffness (characterized by statistical Kuhn length) and develop relationships between these parameters and the known structural features, such as side-chain and backbone degree of polymerization, DP. Bottlebrush polymers are generally described as semi-flexible cylinders with an elongated backbone and side-chains that extend radially from the main-chain. However, a limited number of bottlebrush polymers systems have been studied by SANS and SAXS. Understanding the
conformation of bottlebrushes on a surface and dissolved in solution will lead to better understanding of how to utilize these branched polymers for future applications.

**Figure 1.2** A) SFM image of n-butyl acrylate bottlebrushes showing backbone and side-chain polymer conformation [Sheiko, 2001]⁷. B) AFM of polystyrene bottlebrushes casted from dilute solutions [Xia, 2009]¹⁰. C) AFM height image of poly(vinyl acetate) brushes on a mica substrate [Nese, , 2010]⁸. D) TEM image of core-shell tri-block bottlebrush copolymers. [Li, 2011]⁹. Scale bars (A) 70 nm, (B-D) 100 nm.

1.1.1 Bottlebrush Polymer Synthesis

The densely packed side-chains create steric repulsion around the backbone polymer, making synthesis challenging. Bottlebrush polymers were first synthesized in the early 1980’s ¹²,¹³, and since then there have been vast improvements in making well-defined bottlebrushes. There are three general synthetic methods to synthesize bottlebrush polymers: grafting-to, grafting-from and grafting-through (Figure 1.3)¹⁴,¹⁵. In the grafting-through method, first a “macromonomer” polymer (MM) is synthesized with a mono-functional end group that is polymerizable, such as an acryloyl¹⁶-¹⁹ or norbornene²⁰-²⁵ unit. The second step is polymerization of the macromonomer side-chains. Of the three, only “grafting-through” guarantees full characterization of side-chains and 100 % grafting density. Typically the maximum backbone degree of
polymerization is limited by the molecular weight and type of the side-chain polymer\textsuperscript{14}. Additionally, the low concentration of polymerizable end groups and high steric hindrance of the propagating chain end may result in polymerizations that fail to achieve high conversions. For these reasons backbone DPs by “grafting-through” are limited to < 400 in most cases. Advances in controlled radical polymerization and ring-opening polymerizations have resulted in bottlebrush materials with narrowly dispersed molecular weight distributions and the ability to target backbone and side-chain lengths.

Figure 1.3 Grafting-through, grafting-to and grafting- from synthesis of bottlebrush polymers [Sheiko, 2008]\textsuperscript{14}.

Grafting-through polymerization of bottlebrush polymers is commonly achieved by ring-opening polymerization (ROMP) of a terminal norbornenyl group. Grubb’s ruthenium based catalyst is used to initiate the ROMP of norbornene groups and has been shown to have improved control over a wide variety of macromonomers. Backbone degree of polymerization is determined by the molar ratio of side-chains to catalyst [MM]/[Catalyst]. Gel permeation chromatography (GPC) traces for various
[MM]/[catalyst] ratios are shown in Figure 1.4, where shorter elution time represents higher molecular weight polymers. Backbone DPs have been reported to exceed 400, but long backbone DPs often result in chain termination and broader molecular weight distributions.

**Figure 1.4** Controlled synthesis by grafting-through macromonomers formed by “click chemistry” demonstrating high conversions of macromonomers [Xia, 2009].

Controlled radical polymerization (CRP) methods such as atom transfer radical polymerization (ATRP) 26-30, reversible addition-fragmentation transfer (RAFT) 20,21,26,30,31, and NMP 30 can be initiated with a norbornene functionalized initiator resulting in mono-functional norbornene polymers. The most recently developed CRP mechanism, RAFT, is a versatile and powerful technique 32 to create well-defined macromonomers (Figure 1.5). With a high tolerance for a variety of monomers and mild reactions conditions, polymerization by RAFT has become common in research areas 20,21,30,33. In addition to monomer and initiator, RAFT synthesis requires a chain transfer agent (CTA) (Figure 1.5: iii) that stabilizes and transfers the propagating radical to other polymer chains periodically. An example CTA is a thiocarbonylthio compound composed of S=C(Z)-SR where the “Z” and “R” groups are varied for specific monomer
use\textsuperscript{32}. The R group allows modification and control of polymer end group functionality, an important consideration in the synthesis of macromonomers\textsuperscript{33}.

(i) Initiation

\[ I\rightarrow I \rightarrow 2 I^* \]

\[ I^* \rightarrow M^* \]

(ii) Propagation

\[ M^* \rightarrow P_n^* \]

(iii) Chain Transfer

\[ P_n^* + S-S-R \xrightarrow{k_{add}} P_n-S-S-R \]

\[ P_n-S-S-R \xrightarrow{k_{\beta}} P_n-S-S + R^* \]

(iv) Reinitiation and Propagation

\[ R^* \rightarrow P_m^* \]

(v) Chain Equilibrium

\[ P_m^* + P_n-S-S \rightarrow P_m-S-S-P_n \]

\[ P_m-S-S-P_n \rightarrow S-S-P_m + P_n^* \]

Figure 1.5 RAFT mechanism revealing intermediate steps in reversible addition-fragmentation chain transfer polymerization [Patton, 2006]\textsuperscript{33}.

Macromonomer synthesis via RAFT polymerization is achieved by covalently attaching a norbornene unit to the “Z” group on the CTA. Wooley and coworkers have optimized RAFT polymerization synthesis to preserve the norbornene functionality during polymerization for styrene\textsuperscript{31}, tert-butyl acrylate\textsuperscript{21,31} and methyl-methacrylate\textsuperscript{20} which is typically achieved by low temperatures and low ratio of radical initiator (AIBN). An example of a norbornene-functionalized CTA is shown in Figure 1.6. In order for resulting bottlebrush polymers to be well-defined, it is imperative that macromonomers be mono-functionalized with norbornene end groups\textsuperscript{34}. Utilizing a RAFT-based
approach, a wide-variety of polymer side-chains can be synthesized including random and block copolymer side-chains.

![Chemical structure of norbornene-functionalized CTA for RAFT initiation of macromonomer synthesis](image)

**Figure 1.6** Chemical structure of norbornene-functionalized CTA for RAFT initiation of macromonomer synthesis [Li, 2009].

1.1.2 Bottlebrush copolymers

Bottlebrush copolymers can also be synthesized in a variety of architectures including bottlebrush block copolymers (“blocky”), mixed-arm bottlebrush copolymers, and “core-shell” bottlebrushes (Figure 1.7). Bottlebrush block copolymers, or blocky bottlebrushes, have side-chains that are arranged in distinct “blocks” along the backbone. Blocky bottlebrush polymers, similar to linear block copolymers, can readily self-assemble into large structures in solution or in thin films with large domain spacing. Mixed-arm
bottlebrushes have two or more chemically different homopolymer side-chains that are randomly distributed along the polymer backbone. In the case of core-shell bottlebrush polymers, each side-chain unit is a linear di- or tri-block copolymer. When assembled as a bottlebrush polymer, the inner block (closest to the backbone) becomes the “core” and the outer block polymer becomes the “shell”. Core-shell bottlebrush polymers may be useful for drug encapsulation and medical imaging because small molecules can preferentially bind to the inner core and be shielded from \textit{in vivo} environments by a hydrophilic shell. Recently, bottlebrush polymer research has been focused on developing bottlebrush copolymers for specific applications which we will discuss next.

![Figure 1.7 Structures of bottlebrush copolymers: (A) bottlebrush block copolymers; (B) mixed-arm bottlebrush copolymers; (C) and core–shell bottlebrush copolymers.][Verduzco, 2015]^{35}.

### 1.2 Functional Applications of Bottlebrush Polymers

The unusual branched architecture of bottlebrush polymers leads to a number of novel and potentially useful properties for target applications. For example, unlike linear block copolymers, high molecular weight bottlebrush block copolymers do not entangle and can self-assemble to form structures with large domain sizes, up to several hundred
Bottlebrush block copolymers form micelles in a selective solvent, but have a much lower critical micelle concentration compared with linear diblock copolymers and surfactants, thereby enabling applications such as detection or sensing in biological media that require dilute conditions. Target applications for bottlebrush polymers can be grouped into four general categories: single bottlebrushes in solution, bottlebrush assemblies in solution, thin film assemblies, and bulk assemblies. Applications of bottlebrush copolymers include nanocarriers for drug delivery, stimuli-responsive coatings\textsuperscript{11}, photonics, and lithographic patterning\textsuperscript{36–38}.

The self-assembled structures of bottlebrush copolymers have been studied for a number of bottlebrush systems. High molecular weight polystyrene (PS)-poly(lactic acid) (PLA) blocky bottlebrushes were shown to have 100 – 200 nm cylindrical domains\textsuperscript{39}. Blocky bottlebrushes with up to four side-chain blocks have been synthesized by Bowden and coworkers\textsuperscript{40,41}. The bulk self-assembly of blocky bottlebrushes into lamellar\textsuperscript{39,42–44} and cylindrical\textsuperscript{45,46}domains\textsuperscript{42,43} has also been reported. Xia \textit{et al.} studied the self-assembly behavior of blocky and mixed-arm bottlebrush copolymers prepared by ROMP and found that while both form lamellar structures, blocky bottlebrush lamella are perpendicular to the backbone and mixed arm bottlebrushes form lamellar parallel to the backbone (Figure 1.8)\textsuperscript{10}. Russell and coworkers have also demonstrated that bottlebrush copolymers self-assemble much more rapidly that liner diblock copolymers\textsuperscript{47,48}.

\textbf{Figure 1.8} Blocky and mixed-arm bottlebrush polymers self-assemble into lamellar phases in bulk and thin films [Xia, 2009]\textsuperscript{10}. 

9
Blocky bottlebrush polymers form domain sizes much larger than those observed in linear block copolymers which are advantageous for applications such as photonic crystals and nanolithography patterning. Domain spacing of over 100 nm are ideal materials for use as photonic crystals. Bottlebrush copolymer films have been reported to reflect blue or green light in films and melts\(^{40,49,50}\) (see example in Figure 1.8). Sveinbjörnsson et al. tuned the reflection bands of blocky PS-PLA bottlebrush polymers from 200 – 600 nm by changing the bottlebrush molecular weight \(^{51}\). Poly(isocyanate) based bottlebrushes have been shown to have a broad range of reflection bands (200 – 1200 nm) \(^{52}\). Wooley et al has demonstrated the use of blocky bottlebrush polymers with a low surface-energy component to create patterned photoresist materials with features as small as 10 nm \(^{36-38} \).

Medical applications for bottlebrush polymers in solution include encapsulation, delivery, signaling, and detection. The size and shape of bottlebrush polymers for biomedical applications is an important consideration in material design. The cylindrical shape of many single bottlebrush polymers may be advantageous for increasing in vivo retention time and for cellular uptake \(^3,53\). Assemblies from bottlebrush polymers have also been studied for drug delivery and encapsulation (Figure 1.9). Johnson et al developed a series of water-soluble bottlebrush polymers with bivalent side-chains with covalently bound anti-cancer drugs (doxorubicin)\(^{24,25}\). A variety of core-shell bottlebrush polymers have been synthesized for medical nanocarriers. Core-shell bottlebrushes with degradable PLA cores were prepared by grafting-from \(^{54,55}\), triblock side-chains capable of cylindrical self-assembly \(^9\) and helical polypeptide backbones\(^{56}\) have also been reported. The first core-shell bottlebrush to report enhanced drug-release properties loaded doxorubicin into a poly(carprolactone) (PCL) core (Figure 1.9, C) \(^{57}\).
Figure 1.9 (A) Synthesis of bivalent PEG and doxorubicin bottlebrush polymers [Johnson, 2010]25. (B) schematic of PEG bottlebrush polymer with UV-active release of drug molecules [Johnson, 2010]24 and (C) Doxorubicin release profile from core-shell bottlebrush polymer with PCL core and PEG shell [Du, 2009]57.

An emerging area of interest for drug delivery and biodetection are the micelle assemblies of bottlebrush copolymers, which are typically much larger than linear diblock assemblies. Micelle assemblies of amphiphilic blocky bottlebrushes can have diameters over 100 nms, which would avoid accumulation in the liver58. Other structures, such as cylinders and bilayered have also been observed (Figure 1.10A,
Preliminary studies with bottlebrush polymers have demonstrated use for high-contrast imaging nanoparticles \textit{in vivo} and in biodetection assays.

\textbf{Figure 1.10} A, B) Cryo-TEM images of self-assembled structures from blocky PLA-PEG bottlebrush polymers showing diagram and (A) TEM image for spherical micelles and (B) TEM image for cylindrical micelle assemblies [Fenyves, 2014]. C) Accumulation of labeled bottlebrush polymers at tumor site and liver [Miki, 2011].

\section*{1.3 References}

(1) Ayres, N. \textit{Polymer Chemistry} \textbf{2010}, \textit{1}, 769.


1994, 27, 1662.

(18) Gerle, M.; Fischer, K.; Roos, S.; Müller, A. H. E.; Schmidt, M.; Sheiko, S.

1990, 23, 5201.

(20) Li, A.; Ma, J.; Sun, G.; Li, Z.; Cho, S.; Clark, C.; Wooley, K. L. J. Polym.


(22) Breunig, S.; Héroguez, V.; Gnanou, Y.; Fontanille, M. Macromolecular
Symposia 1995, 95, 151.

(23) Mecerreyes, D.; Dahan, D.; Lecomte, P.; Dubois, P.; Demonceau, A.;

(24) Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Lim, Y.-H.; Finn, M. G.;
559.

(25) Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Xia, Y.; Durrell, A. C.; Tirrell, D.

(27) Cheng, G.; Böker, A.; Zhang, M.; Krausch, G.; Müller, A. H. E. 


(34) Teo, Y. C.; Xia, Y. *Macromolecules* **2015**.


(41) Yoo, J.; Runge, M. B.; Bowden, N. B. *Polymer* **2011**, *52*, 2499.


2. Small-Angle Neutron Scattering Analysis of Bottlebrush Polymers made by Grafting-Through Polymerization

[The work described in this chapter is published in: Stacy L. Pesek, Xianyu Li, Boualem Hammouda, Kunlun Huong, Rafael Verduzco, “Small-Angle Neutron Scattering Analysis of Bottlebrush Polymers made by Grafting-Through Polymerization” Macromolecules, 2013, 46, 6998-7005.]

2.1 Abstract

Bottlebrush polymers are highly branched macromolecules with potential applications for anti-fouling coatings, rheological modifiers, and drug delivery systems. However, the solution conformation of bottlebrush polymers has been studied in only a limited set of materials made primarily by grafting-from polymerization. Here we present small-angle neutron scattering (SANS) measurements on a series of polystyrene bottlebrush polymers with varying side-chain and backbone lengths in d8-toluene to analyze the size, shape, and conformation. Bottlebrush polymers with 2 - 6 kg mol⁻¹ polystyrene side-chains (degree of polymerization DP = 14 - 54) and poly(oxa-norbornene) backbones (DP = 10 - 264) were synthesized using a reversible addition-fragmentation chain-transfer (RAFT) then (ROMP) grafting-through synthetic scheme, which guarantees full side-chain attachment. Absolute molecular weights for the side-chains and overall bottlebrush polymers are determined by a combination of static light scattering and ¹H NMR measurements. Analysis by Gunier-Porod, rigid cylinder, and flexible cylinder models provided estimates for bottlebrush polymer length, radius, and stiffness. Consistent with prior measurements, bottlebrush polymer cross-sectional area depends primarily on side-chain DP, and the radius of gyration, \( R_g \), exhibits a power-law dependence with side-
chain DP. We also observe a sphere-to-cylinder transition with increasing backbone DP, with the transition occurring at approximately a backbone DP of 120 for the polystyrene bottlebrush polymers studied. This indicates that cylindrical form factors are inappropriate for bottlebrush polymers with short backbone DPs, and a combination of spherical and cylindrical form factor models provide a comprehensive analysis. The maximum molecular dimension for the series studied varies from 25 up to 350 nm. Transmission electron micrographs reveal only spherical particles with sizes ranging from 25-45 nm, suggesting TEM measurements are a poor reflection of solution conformations.

2.2 Introduction

Bottlebrush polymers are highly branched macromolecules with polymeric side-chains attached to a main-chain polymer backbone (Figure 2.1) and are promising for applications that rely on large, highly extended macromolecules and/or densely packed polymeric chains. These include stimuli-responsive surfaces, polymer photonics, and drug delivery systems\(^1{-8}\). The development of bottlebrush polymers for applications such as drug delivery requires quantitative knowledge of their structure \textit{in solution}, but the majority of work with bottlebrush polymers has relied on characterization of bottlebrush polymers adsorbed to a surface or in the melt state. This can provide an estimate of single-molecule size but not quantitative information on their solution-state structure. Here, we present a detailed analysis of the conformation of a model series of bottlebrush polymers in solution through small-angle neutron scattering (SANS) measurement and analysis.

Three general techniques to synthesize bottlebrush polymers include grafting-from\(^9{-12}\), grafting-to\(^13,14\) and grafting-through\(^2,15{-17}\). The grafting-from approach has been the most widely used\(^15,18,19\) and can give large and synthetically diverse bottlebrush polymers, but with imperfect side-chain attachment\(^9,12,20\). The grafting-to technique yields varying degrees of grafting efficiencies\(^21,22\). Of the three methods, grafting-through is the only technique that guarantees 100% side-chain attachment. Recent work has demonstrated that living ring-opening metathesis polymerization (ROMP) of norbornenyl macromonomers can be used to prepare well-defined bottlebrush polymers with
controlled backbone and side-chain molecular weights\textsuperscript{23,24}. While a variety of bottlebrush polymers made by the ROMP grafting-through technique have been reported recently, a study of their solution size and conformation has not been reported. Prior small-angle X-ray scattering (SAXS) and SANS studies have focused on bottlebrush polymers prepared by the grafting-from technique. Additionally, previously reported studies focused on a limited set of materials with typically long backbone degrees of polymerization (DPs) and in some cases neglected to measure the absolute molecular weight of both the side-chains and polymeric backbone, which is necessary for quantitative analysis and comparison between studies.

**Figure 2.1** Schematic for a bottlebrush polymer. The schematic depicts an extended, cylindrical bottlebrush polymer with fully stretched polymeric side-chains.

Herein, we present SANS studies of bottlebrush polymers in solution with systematically varied backbone and side-chain lengths. In contrast to previous SAXS and SANS studies of bottlebrush polymers\textsuperscript{15,18}, we focus on bottlebrush polymers made \textit{via} a grafting-through approach. Absolute molecular weights for the side-chains and overall bottlebrush polymers are determined by a combination of static light scattering and \textsuperscript{1}H NMR measurements. SANS data are analyzed by a Gunier-Porod and cylindrical form factor models to estimate the radius of gyration, elongation, diameter, and persistence length of the bottlebrush polymers in solution. Our SANS measurements and analysis find a power-law dependence of the bottlebrush polymer cross-sectional area with side-chain DP, in quantitative agreement with previous studies. We find a sphere-to-cylinder transition that has not been previously reported in previous experimental measurements but is consistent with predictions of recent multi-scale molecular simulations of bottlebrush polymers\textsuperscript{25}. Temperature changes result in small but significant changes to the overall size of the bottlebrush polymer, and we demonstrate that transmission electron
microscopy (TEM) measurements of bottlebrush polymers adsorbed to a surface are a poor reflection of the size and shape of bottlebrush polymers in solution.

2.3 Experimental

2.3.1 Materials

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used as received. Styrene was passed through a basic alumina column to remove inhibitor before polymerization. Dichloromethane (CH$_2$Cl$_2$) was dried over molecular sieves (4Å). Exo-7-oxaicyclo(2,2,1) hept-5-ene 2-3 dicarboxylic anhydride (oxa-norbornene) and 4-(2-Hydroxyethyl)-10-oxa-4-azatriacyclo[5.2.1.0$^{2,6}$]dec-8-ene-3,5-dion(oxa norbornene ethanol) (NbCTA, 1) were prepared as previously described and purified by recrystallization $^{26}$. Modified Grubb’s catalyst (H$_2$IMes)(pyr)$_2$(Cl)$_2$RuCHPh was synthesized as previously described $^{27}$.

![Scheme 2.1: Synthesis of PS macromonomers by reversible addition-fragmentation chain-transfer (RAFT) followed by grafting-through synthesis of PS bottlebrush polymers via ring-opening metathesis polymerization (ROMP). The final PS bottlebrush](image)

Scheme 2.1: Synthesis of PS macromonomers by reversible addition-fragmentation chain-transfer (RAFT) followed by grafting-through synthesis of PS bottlebrush polymers via ring-opening metathesis polymerization (ROMP). The final PS bottlebrush
Polymers PNB(PSN)M have PS side-chains with a degree of polymerization $N$ and backbone with a degree of polymerization $M$.

**Norbornene-functionalized Polystyrene Macromonomer (NBPSN, 2) via RAFT**

Synthesis is modified from our previous report$^2$6. Optimized reaction conditions for each molecular weight are detailed in supplemental information, and details for the synthesis of NbPS42 are presented here. To a 50mL round bottom flask equipped with a stir bar, NbCTA 1 (0.114g, 0.193mmol) and styrene (6.09g, 58.53mmol) were added, followed by the addition of AIBN (.00323g, 0.0195 mmol). The reaction flask was purged with three freeze-pump-thaw cycles and then heated to 50 °C in a temperature-controlled oil bath. At every hour, an aliquot was taken from the reaction mixture and analyzed by gel permeation chromatography (GPC). After 8.5 hours, the reaction was quenched by cooling the reaction flask in a liquid nitrogen bath and exposing to air. The polymer was precipitated twice in methanol and collected by filtration. Yield: 0.669 g; $M_n$= 4900 g mol$^{-1}$; $M_w/M_n$ = 1.12. Figure 2.2 shows $^1$H NMR spectra.

**Figure 2.2: $^1$H NMR spectra of P(NbPSN)M (3) showing relevant chemical shifts**

**Polystyrene bottlebrushes (PNB(PSN)M**). In a representative procedure, modified Grubb’s second generation catalyst ((H$_2$IMes)(pyr)$_2$Cl$_2$RuCHPh) (0.44 mg, 0.0412 mmol) was dissolved in anhydrous CH$_2$Cl$_2$ in a 5mL round bottom flask equipped with a
stir bar. 2 (0.2025 g, 0.0213 mmol) was added to a separate 5 mL round bottom flask equipped with a stir bar, purged and backfilled with nitrogen three times, and then dissolved in anhydrous CH₂Cl₂ (0.5 mL, 0.05 M). The macromonomer solution was transferred to the stirring catalyst solution via syringe. The solution was allowed to stir for 1 hour at which time the reaction was quenched by the addition of 100 μL butyl vinyl ether. GPC confirmed crude conversion of macromonomer to be greater than 94% for all PS bottlebrush polymers. The product was recovered by precipitating twice in methanol and collecting by filtration. PNb(PS₄₂)₁₄₈: $M_{n, GPC} = 135.4$ kg mol⁻¹, $M_w / M_n = 1.52$. $dn/dc = 0.177$ in THF. $M_{w, LS} = 1100$ kg mol⁻¹.

2.3.2 Instrumentation

**Gel-Permeation Chromatography (GPC).** Polymer molecular weights and molecular weight polydispersities (PDIs) were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10000 Å pore sizes), an Agilent variable wavelength UV/vis detector, a Wyatt technology HELEOS II multangle laser light scattering (MALLS) detector ($\lambda = 658$ nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/vis (SEC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer $dn/dc$ values were calculated assuming 100% mass recovery and correcting the injected mass to account for unreacted macromonomer.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Proton-NMR ($^1$H NMR) spectra were recorded using tetramethylsilane as internal standard in CDCl₃ on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm o.d. tubes with the concentration of 10 mg/mL.

**Small Angle Neutron Scattering (SANS).** Temperature dependent SANS measurements were performed at the National Institute of Standards and Technology Center for Neutron Research on the NG3 30 m instrument with a neutron wavelength $\lambda = 6$ Å. Three sample-detector distances were used (1.3 m, 4 m, and 13 m), which leads to
an overall $q$-range of $0.003 \text{ Å}^{-1} < q < 0.4 \text{ Å}^{-1}$. Polymer samples were prepared at 1 wt \% in deuterated-toluene and allowed to equilibrate at RT for at least 4 hours. Temperature control was provided by a water circulation bath, and the actual sample temperatures were measured using a thermocouple in thermal contact with the samples. Samples were allowed to equilibrate at each temperature for at least 1 h. For the temperature series data, temperature set points were input as 10 °C, 25 °C, 40 °C, 55 °C, 70 °C, and 85 °C and measured to be 11 °C, 25 °C, 40 °C, 54 °C, 68 °C, and 83 °C, respectively. Scattering data were corrected for solvent baseline with a scale factor (0.95-1.02) appropriate for the mass fraction of solvent. Model fitting was performed using the NCNR Data Analysis IGOR PRO software and the Guinier-Porod, cylinder, and flexible cylinder models.

**Transmission Electron Microscopy (TEM).** TEM was performed on JOEL 2010 TEM. Polymer solutions (0.1-1mg/mL polymer in toluene) were drop cast onto carbon grids and stained with RuO$_4$ for 30-90 minutes prior to imaging.

2.4 Results

2.4.1 Bottlebrush Polymer synthesis.

The grafting-through approach enables the preparation of a systematic series of fully grafted bottlebrush polymers with varying backbone and side-chain lengths. As shown in Scheme 1, polystyrene (PS) bottlebrush polymers are prepared in two steps. First, PS macromonomers NbPS$_N$ (2) with degree of polymerization $N$ are synthesized via RAFT using a norbornene-functionalized chain-transfer agent (NbCTA 1). PS bottlebrush polymers are subsequently prepared by ROMP of NbPSN macromonomers. The resulting PS bottlebrush polymers have side-chain molecular weights $M_w$ ranging from 3.1 - 6.9 kg mol$^{-1}$, corresponding to side-chain DPs from 14 to 54, and overall molecular weights from 36 to 3,140 kg mol$^{-1}$, corresponding to backbone degrees of polymerization DP from 10 to 250 (Table 1). Bottlebrush polymer polydispersities (PDI) range from 1.2 to 2.3, with broader molecular weight distributions for larger PS side-chains.

We note that the side-chains are separated by 4 carbon atoms of the bottlebrush polymer backbone, roughly double the separation between grafted chains previously analyzed by SAXS and SANS$^{18,33-35}$. Also, all bottlebrush polymer side-chains are
terminated by a trithiocarbonate chain-transfer agent (CTA) end-groups. Although the scattering length density contrast for the trithiocarbonte group relative to d₈-toluene is greater than that for a styrene monomer, that mass content is relatively small. For the shortest PS side-chain with a DP of 14, the mass-content of the trithiocarbonate endgroup is roughly 8 wt %. Differences in the scattering length density of the endgroup and styrene repeat unit are neglected in the modeling and analysis of SANS data.

Table 2.1: Properties of PS bottlebrush polymers PNb(PSN)M, where N denotes the side-chain DP and M the backbone DP.

<table>
<thead>
<tr>
<th>Side-chain</th>
<th>Bottlebrush</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb(PS14)45</td>
<td>2.3</td>
<td>14</td>
<td>1.15</td>
<td>105.0</td>
<td>45</td>
<td>1.16</td>
</tr>
<tr>
<td>PNb(PS14)264</td>
<td>2.3</td>
<td>14</td>
<td>1.15</td>
<td>881.0</td>
<td>16.2</td>
<td>260</td>
</tr>
<tr>
<td>PNb(PS20)11</td>
<td>3.1</td>
<td>20</td>
<td>1.18</td>
<td>36.6</td>
<td>28.3</td>
<td>11</td>
</tr>
<tr>
<td>PNb(PS20)15</td>
<td>3.1</td>
<td>20</td>
<td>1.18</td>
<td>63.0</td>
<td>73.0</td>
<td>15</td>
</tr>
<tr>
<td>PNb(PS24)120</td>
<td>3.6</td>
<td>24</td>
<td>1.16</td>
<td>453.0</td>
<td>19.9</td>
<td>120</td>
</tr>
<tr>
<td>PNb(PS42)148</td>
<td>5.6</td>
<td>42</td>
<td>1.14</td>
<td>1100.0</td>
<td>135.0</td>
<td>150</td>
</tr>
<tr>
<td>PNb(PS54)216</td>
<td>6.9</td>
<td>54</td>
<td>1.12</td>
<td>3140.0</td>
<td>77.9</td>
<td>220</td>
</tr>
</tbody>
</table>

- **a.** Mₜ by GPC relative to monodisperse PS standards. Measured values are in good agreement with ¹H NMR measurements (Table 2.2).
- **b.** from GPC relative to monodisperse PS standards
- **c.** Mₛ calculated from GPC-light scattering analysis
- **d.** Calculated using number-averaged molecular weights Mₙ for side-chains and bottlebrush polymer
- **e.** from GPC relative to monodisperse PS standards
Table 2.2: Optimized reaction conditions for RAFT-based polystyrene macromonomer synthesis

<table>
<thead>
<tr>
<th>Sidechain</th>
<th>$M_n$</th>
<th>$M_n/M_w$</th>
<th>$[\text{NbCTA}]:[\text{AIBN}]:[\text{Styrene}]$ (mol)</th>
<th>$T$ (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbPS14</td>
<td>2021</td>
<td>1.15</td>
<td>1 : 1/360 : 225</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>NbPS20</td>
<td>2593</td>
<td>1.18</td>
<td>1 : 1/400 : 170</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>NbPS24</td>
<td>3123</td>
<td>1.16</td>
<td>1 : 1/764 : 247</td>
<td>50</td>
<td>115</td>
</tr>
<tr>
<td>NbPS42</td>
<td>4917</td>
<td>1.12</td>
<td>1 : 1/10 : 300</td>
<td>65</td>
<td>8.5</td>
</tr>
<tr>
<td>NbPS54</td>
<td>6138</td>
<td>1.12</td>
<td>1 : 1/10 : 256</td>
<td>75</td>
<td>6</td>
</tr>
</tbody>
</table>

For quantitative SANS analysis, accurate measurements of the absolute molecular weight of bottlebrush polymers and bottlebrush polymer side-chains are needed. PS side-chain molecular weight and PDI was obtained by size-exclusion chromatography analysis calibrated by a set of monodisperse PS standards. Measured values were in good agreement with $^1$H NMR measurements of side-chain DP (see Figure 2.2 and Table 2.2). The absolute molecular weight of bottlebrush polymers was measured by static light scattering measurements. The use of a linear PS calibration curve significantly underestimates the true molecular weight of PS bottlebrush polymers (see Supporting Information Table 2.1). This reflects the more compact structure of PS bottlebrush polymers in solution compared with linear PS of a comparable molecular weight.

2.4.2 Small-angle Neutron Scattering (SANS) Measurements and Analysis.

SANS measurements were carried out on solutions of bottlebrush polymer at 1 wt % in deuterated toluene ($d_8$-tol), a good solvent for the polystyrene side-chains and polynorbornene backbone. SANS analysis was performed over a $q$-range of 0.008 Å$^{-1}$ up to approximately 0.4 Å$^{-1}$. This broad $q$-range provides information on the structure of bottlebrush polymers at multiple length scales. Roughly, the low-$q$ region ($q = 0.008 – 0.02$ Å$^{-1}$) gives information on the overall size of the bottlebrush polymer, the mid-$q$ region ($q = 0.02 – 0.1$ Å$^{-1}$) provides information about the cross sectional size and
stiffness, and the high-q region \((q > 0.1 \text{ Å}^{-1})\) is indicative of thermal fluctuations at the molecular level.

Figure 2.3: SANS scattering intensity for 2.3 - 3.6 kg mol\(^{-1}\) side-chain bottlebrush polymers (top) and for bottlebrush polymers with long backbones (backbone DP > 100) and varying side-chain lengths (bottom). Polymers with similar cross-sectional areas (~\(R\)) overlap in the mid-q region \((0.02 > q > 0.1)\). Intensity at low \(q\) \((q < 0.02)\) increases with larger backbone DP indicating larger overall size.

A comparison of the scattered intensity for bottlebrush polymers with varying side-chain lengths and backbone lengths provides qualitative information about bottlebrush polymer size and cross-sectional area. As shown in Figure 2.3, the SANS data for a series of bottlebrush polymers with similar side-chain lengths \((\text{DP} \sim 18 \pm 4)\) and varying backbone lengths \((\text{DP} = 11 - 264)\) overlap in the mid-q region but diverge in the low-q region, with larger bottlebrush polymers exhibiting increased low-q scattering intensity. This indicates qualitatively that the series of bottlebrush polymers have similar cross-sectional area and stiffness but differ in overall size. For a series of bottlebrush polymers
with long backbone lengths and varying side-chain lengths, differences in the neutron scattered intensity is observed in the low-\(q\) and mid-\(q\) regions, indicating that both cross-sectional area and overall size changes for this series of polymers.

The slope at low-\(q\) provides information on polymer conformation. Plateaus indicate globular or spherical particles, as observed for PNB(PS\(20\))15. Alternatively, an increasing slope at low-\(q\) indicates an elongated shape. PNB(PS\(14\))264 and PNB(PS\(54\))216 have the greatest backbone DP, and the slope in the low-\(q\) region of the scattered intensity indicates qualitatively they are more elongated in solution compared with the rest of the series. In some cases, such as PNB(PS\(24\))120, a sharp upturn at very low-\(q\) (\(q < 0.07\)) reflects the presence of polymer aggregates. For example both PNB(PS\(20\))15 and PNB(PS\(14\))264 exhibit small degrees of aggregation in solution. In all cases, the amount of aggregation is minor and the data can be fit to a model for a single molecular form factor.

Figure 2.4: Poly(PS\(14\))45 SANS data and model fits for Guinier-Porod (GP fit), rigid cylinder (Cyl) and flexible cylinder (FlexCyl) models. All models are fit between \(0.004 < q < 0.09\).

In order to get a quantitative measure of bottlebrush solution size and conformation, SANS data were first fit to a Guinier-Porod model\(^\text{29}\) (Figure 2.4). This is an empirical model applicable to objects of arbitrary shape and provides an estimate of the radius of gyration, \(R_g\), and dimension parameter, \(s\). The empirical model for Guinier-Porod is represented by the following equations:
\[ I(Q) = \frac{G}{Q^2} \exp \left[ -\frac{Q^2 R_g^2}{3-s} \right] \text{ for } Q \leq Q_1 \]  
(Eqn. 2.1)

\[ I(Q) = \frac{D}{Q^m} + B \text{ for } Q \geq Q_1 \]  
(Eqn. 2.2)

Where \( G \) is a scale factor, \( Q \) is the scatter variable, \( m \) is the Porod exponent and \( D \) and \( Q_1 \) are defined by the following:

\[ D = G \exp \left[ -\frac{Q_1^2 R_g}{3} \right] Q_1^m \]  
(Eqn. 2.3)

\[ Q_1 = \frac{1}{R_g} \sqrt{\frac{3m}{2}} \]  
(Eqn. 2.4)

As shown in Table 2.3, results from Gunier-Porod model predict \( R_g \) values in the range of 28 – 49 Å for PS bottlebrush polymers studied. This is much smaller than expected for the bottlebrush polymers with large backbone DPs but is consistent with the expected cross-sectional area. As shown in Figure 2.5 and Table 2.3, the \( R_g \) estimate from the Gunier-Porod model trends with the side-chain DP but is independent of the backbone DP. From this, we conclude that the \( R_g \) value from the Gunier-Porod model reflects the cross-sectional area and provides an estimate of the bottlebrush polymer radius, not the overall size of the molecule. This is further supported by comparison with model fitting using cylindrical form factors, discussed below.

The dimension parameter \( s \) reflects the shape of the molecule: \( s = 0 \) corresponds to a spherical molecule while \( s = 1 \) indicates that the molecule is elongated or rod-like. As shown in Figure 2.5 and Table 2.3, the dimension parameter is roughly 0.1 for bottlebrush polymers with short backbones (DP < 120) but increases significantly with backbone DP greater than 120. The dimension parameter \( s \) increases from 0.1 to 0.7 as the backbone DP increases from 120 to 250. Thus, the Guinier-Porod model indicates an increasing bottlebrush polymer radius with increasing side-chain molecular weight and increasing polymer elongation with backbone repeat units (Figure 2.5).
Table 2.3: Results from Guinier-Porod model

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_g$ [Å]</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb(PS14)45</td>
<td>34.2 ± 0.2</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS14)264</td>
<td>27.2 ± 0.3</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS20)11</td>
<td>28.3 ± 0.3</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS20)15</td>
<td>27.9 ± 0.3</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS24)120</td>
<td>31.3 ± 0.3</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS42)148</td>
<td>44.3 ± 0.2</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>PNb(PS54)216</td>
<td>48.9 ± 0.3</td>
<td>0.52 ± 0.01</td>
</tr>
</tbody>
</table>
Figure 2.5: Analysis by the Guinier-Porod model indicates an increase in radius of gyration, \( R_g \), with side-chain length (top) and a strong increase in the dimension parameter, \( s \), as a function of backbone length for backbone DPs greater than 150 (bottom). Standard deviations (shown) are smaller than data points.

More detailed information on bottlebrush polymers can be extracted using rigid and flexible cylinder models for the scattering form factor\(^{28}\). The former model approximates individual bottlebrush polymers as rigid cylinders in solution while the latter assumes they are flexible cylinders, characterized by a Kuhn step length \( \lambda_k \). The rigid cylinder model gives an estimate for the radius, \( R \), and length, \( L \), only, while the flexible cylinder model gives an estimate of the radius, \( R_c \), in addition to contour length, \( L_c \), and Kuhn step length, \( \lambda_k \). The rigid cylinder model is described by the following function:

\[
P(q) = \frac{\theta}{V_{cyl}} \int_0^{\pi/2} f^2(q, \alpha) \sin \alpha \, d\alpha
\]  

(Eqn. 2.5)
\[ f(q, \alpha) = 2(\rho_{cyl} - \rho_{solv})v_{cyl}j_0(qH\cos\alpha)\frac{j_1(qr \sin\alpha)}{qr \sin\alpha} \]  

(Eqn. 2.6)

Where \( V_{cyl} = \pi r^2 L \), \( J_0 = \sin(x)/(x) \), \( J_1 \) is a first order Bessel function, and \( \alpha \) is defined as the angle between the cylinder axis and the scatter vector, \( q \).

The flexible cylinder model \(^{31,32}\) is described by the following function:

\[
S_{exy}(q) = \left( 1 - w(qR_g) \right) S_{Debye}(q, L, b)
+ w(qR_g) \left[ C_1(qR_g)^{-1/v} + C_2(qR_g)^{-2/v} + C_3(qR_g)^{-3/v} \right]
\]  

(Eqn. 2.7)

The flexible cylinder model has been used in previous SANS and SAXS studies of bottlebrush polymers\(^{15,18,33}\). Results from analysis of the SANS data by cylinder and flexible cylinder models are shown in Table 2.4 and Figure 2.6. The cylinder models are in good agreement, with a longer contour length \( L_c \) for the flexible cylinder model compared with the length \( L \) of the rigid cylinder model, as expected. The radii range from roughly 25 – 50 Å and increase with side-chain DP, consistent with the \( R_g \) values from Guinier-Porod model.
**Table 2.4: Results from rigid cylinder and flexible cylinder models**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb(PS14)45</td>
<td>31.1 ± 0.2</td>
<td>110.5 ± 0.6</td>
<td>27.8 ± 0.2</td>
<td>155.2 ± 2.8</td>
<td>66.9 ± 2.0</td>
</tr>
<tr>
<td>PNb(PS14)264</td>
<td>28.9 ± 0.1</td>
<td>443.0 ± 5.5</td>
<td>25.1 ± 0.2</td>
<td>454.6 ± 6.2</td>
<td>113.3 ± 3.7</td>
</tr>
<tr>
<td>PNb(PS20)11</td>
<td>26.7 ± 0.3</td>
<td>91.3 ± 0.8</td>
<td>24.8 ± 0.3</td>
<td>123.8 ± 2.9</td>
<td>54.3 ± 2.4</td>
</tr>
<tr>
<td>PNb(PS20)15</td>
<td>25.7 ± 0.4</td>
<td>101.8 ± 0.9</td>
<td>22.9 ± 1.0</td>
<td>155.9 ± 7.3</td>
<td>51.1 ± 7.1</td>
</tr>
<tr>
<td>PNb(PS24)120</td>
<td>29.6 ± 0.3</td>
<td>104.0 ± 0.9</td>
<td>27.4 ± 0.3</td>
<td>146.1 ± 3.6</td>
<td>58.4 ± 3.2</td>
</tr>
<tr>
<td>PNb(PS42)148</td>
<td>42.1 ± 0.2</td>
<td>163.5 ± 0.9</td>
<td>36.5 ± 0.7</td>
<td>275.1 ± 26.6</td>
<td>68.8 ± 12.1</td>
</tr>
<tr>
<td>PNb(PS54)216</td>
<td>51.6 ± 0.1</td>
<td>367.8 ± 2.1</td>
<td>42.7 ± 0.3</td>
<td>516.8 ± 10.8</td>
<td>129.1 ± 5.8</td>
</tr>
</tbody>
</table>

The rigid cylinder length \( L \) and contour length \( L_c \) are both highly dependent on the backbone DP with a strong increase above a backbone DP of approximately 120. Below DP of 90, the cylinder lengths are roughly independent of backbone DP. This is inconsistent with a cylindrical shape for bottlebrush polymers in solution and suggests side-chain extension is comparable to the end-to-end distance of the bottlebrush polymer backbone. This is also predicted by the Gunier-Porod model which gives a small dimension parameter \( s \) for all bottlebrush polymers with backbone DPs less than 120. We note that for these samples the values of the Kuhn length \( \lambda_k \) predicted from the flexible cylinder model are equal to twice the cylinder radius; equivalently, the bottlebrush polymer persistence length \((2l_p = \lambda_k)\) is roughly equal to the bottlebrush polymer radius. This suggests a spherical globule conformation of the bottlebrush polymer overall, not an extended cylinder.
The flexible cylinder model predicts much larger Kuhn lengths $\lambda_k$ for bottlebrush polymers with larger backbone DPs. For the two more extended bottlebrush polymers studied - PNb(PS14)264 and PNb(PS54)216 – $\lambda_k$ increases weakly with increasing side-chain length; $\lambda_k$ increases by 13% with an almost 4 times increase in the side-chain DP. Although we cannot draw strong conclusions based on two samples, we note that molecular simulations predict a modest increase in persistence length with increasing side-chain DP$^{25}$.

![Graph showing the relationship between side-chain length and various properties of the bottlebrush polymers](image)

**Figure 2.6:** Results from cylinder (□) and flexible-cylinder (○) models are shown. Radii, $R$, (top) increase with side-chain length. Length, $L$, (□) and contour length, $L_c$, (○) (bottom) are dependent on backbone length. Standard deviations (shown) are typically smaller than data points.
The changes in the bottlebrush polymer radius and overall size were measured as a function of temperature to determine how the side-chain and backbone conformation changes with solvent quality. Five bottlebrush polymers were analyzed at 11 °C, 25 °C, 40 °C, 54 °C, 68 °C, and 83 °C in d8-toluene, a roughly athermal solvent for polystyrene for the measured temperature range and are shown in Figure 2.7. Linear PS in toluene shows a weak temperature dependence of the intrinsic viscosity with temperature in toluene, with increased chain swelling at elevated temperatures. For cylindrical bottlebrush polymers (PNb(PS24)120 and PNb(PS54)216), we observed modest backbone elongation with increasing temperature, between 3 – 7% increases in length, as determined from rigid cylinder models (Figure 2.8). Radii of bottlebrush polymers remained relatively constant with increasing temperature.

Figure 2.7: SANS data collected for 10 °C, 25 °C, 40 °C, 55 °C, 70 °C, and 85 °C for poly(PS14)45 (A.), poly(PS20)15 (B.), poly(PS24)120 (C.), and poly(PS54)216 (D.).
Figure 2.8: Normalized length (solid markers) and dimension parameter (open markers) for bottlebrush polymers (top), and cylinder radii (solid markers) and Guinier-Porod $R_g$ (open markers). Bottlebrush polymers with backbone DPs greater than 100 (PNb(PS24)120 and PNb(PS54)216) were analyzed by the cylinder model while shorter bottlebrush polymers PNb(PS14)45 and PNb(PS20)15 were analyzed by the Guinier-Porod model. PNb(PS24)120 and PNb(PS54)216 show modest elongation with increasing temperature. Values for length, $L_c$, radius, $R$, and radius of gyration, $R_g$, are normalized with respect to the average length or radius for each polymer; error bars represent model fit tolerance.

2.4.2 TEM Analysis.

For comparison to the bottlebrush polymer sizes calculated from SANS analysis, select bottlebrush polymers were visualized by conventional TEM. As shown in Figure 2.9,
TEM reveals particles that are spherical in shape. Bottlebrush polymers with longer backbone DPs (PNb(14)264 and PNb(54)216) have a more ellipsoidal shape, but no cylindrical molecules are observed. Precise quantitative values are difficult to extract from TEM analysis, but image analysis provided estimates for the average molecular diameter. Particle size measurements by TEM gave larger values for average molecular size compared with SANS measurements. For example, PNb(PS20)15 and PNb(PS14)264 lengths were measured to be approximately 22 nm and 43 nm in length by TEM compared to 10 and 44 nm by SANS.

Figure 2.9: TEM micrographs of select PS bottlebrush polymers adsorbed to a surface. Scale bars (shown) are 100 nm.

2.5 Discussion

The measurements reported here provide quantitative information on the solution conformation of bottlebrush polymers. Consistent with previous SANS and SAXS measurements, we observe a power-law dependence of the size-of the side-chains with side-chain DP, \( R \sim \text{DP}^\nu \). Using \( R_g \) values from the Gunier-Porod model, the value of the exponent \( \nu \) is 0.39. Using cylinder radius \( R \) from the cylindrical form factor models provides a slightly larger exponent 0.42. As noted above, SANS data have a contribution from the trithiocarbonate CTA pendant on each side-chain. The effect of the CTA will be more pronounced for shorter side-chains. Neglecting the bottlebrush polymers with the shortest PS side-chain DPs, we find exponents of 0.57 and 0.71 from Gunier-Porod and cylindrical form factor models. These numbers are consistent with previous studies and
suggest a 2-D or 3-D self-avoiding walk conformation of the polymeric side-chains. 

Additionally, we can estimate the length per repeat unit for the polystyrene side-chains using the side-chain DP and values for $R$ or $R_g$. Side-chains show an average length per repeat unit greater than 1 nm in all cases, indicating they are strongly stretched.

Analysis of SANS data by both Guinier-Porod and cylindrical form factor models predict a sphere-to-cylinder transition with increasing backbone DP, shown schematically in Figure 2.10. The data for PS bottlebrush polymers show a more elongated solution conformation for PS bottlebrush polymers with DPs greater than 120, while bottlebrush polymers with smaller backbone DPs are roughly spherical globules in solution. This is consistent with recent molecular simulations \textsuperscript{25} and previous experimental observations\textsuperscript{24,38}. While recent SANS and SAXS studies have focused on bottlebrush polymers with backbone DPs greater than 180, early studies of bottlebrush polymers prepared by free-radical polymerization concluded bottlebrush polymers become more extended for backbone degrees of polymerization greater than 10\textsuperscript{34}. Other examples include bottlebrush polymers with short backbone and side-chain DPs analyzed by SANS and TEM measurements of bottlebrush polymers made by grafting-through\textsuperscript{24}. Monte-Carlo simulations by Binder et al predict a total radius of gyration $R_g$ comparable to the side-chain size for backbone DPs less than 100.

\textbf{Figure 2.10:} Proposed structure for bottlebrush polymers for small (left) and large (right) backbone DPs. Bottlebrush polymers assume a spherical conformation at low backbone DPs and a more extended conformation at larger backbone DPs.
Thus, the use of a cylindrical form factor is inappropriate for bottlebrush polymers with smaller backbone DPs. As shown in Figure 5, for short backbone DPs cylindrical models predict a molecular length independent of backbone DP, which is inconsistent with a rod-like conformation. We can estimate the maximum dimension for bottlebrush polymers in solution using the Guinier-Porod model (diameter $D = 2\sqrt{2} R_g$) for bottlebrush polymers with backbone DPs less than 120 and the length predictions for bottlebrush polymers with backbone DPs greater than 120 (Figure 2.5). As shown in Figure 2.6, this analysis predicts the maximum dimension is independent of backbone length below backbone DPs of 120, where side-chain stretching determines the size of the bottlebrush polymer. Above a backbone DP of roughly 120, the maximum dimension increases with backbone DP. While we observe this conformational transition at a backbone DP of roughly 120, this transition will generally depend both on side-chain length, flexibility, and grafting density.

Our results further indicate that the backbone is not fully stretched, with lengths of backbone per monomer repeat unit, $l_b$, roughly 0.18 nm ± 0.05 using contour length values from the flexible cylinder model for the bottlebrush polymers with DPs greater than 120. By comparison, the theoretical length for a fully extended backbone of roughly 0.5 nm per backbone unit and the distance between side-chain monomer is estimated to be roughly 1 nm. For bottlebrush polymers with backbone DPs greater than 120, temperature changes are found to only affect the backbone length and not side-chain length or bottlebrush polymer radius. This suggests that side-chains are highly stretched at all temperatures while the backbone has more flexibility and reflects modest elongation with increasing temperature.

TEM analysis gives a poor reflection of the solution conformation of bottlebrush polymers. In all cases, we observe spherical particles ranging in 20 – 40 nm in aspect ratio. The discrepancy between SANS and TEM measurements of molecular size and shape may be due to a combination of effects: molecular aggregation during TEM sample preparation, side-chain collapse, and molecule deformation on adsorption to a solid surface.
2.6 References


3. Structural Properties of Poly(norbornene)-grafted-Poly(lactic acid) Bottlebrush Polymers Determined by SANS

3.1 Introduction

Bottlebrush or molecular brush polymers represent a unique class of highly branched, single molecules. Recent work on bottlebrushes has focused on the single-molecule visualization\(^1\text{-}^3\), rheological properties\(^4\text{-}^7\), complex hierarchical synthesis\(^8\text{-}^9\) and applications of specialized materials\(^10\text{-}^{13}\). Additionally, there is a growing interest in the atomic structural conformation of bottlebrush polymers in solution, which is reflected in an increased number of studies\(^2\text{-}^{13}\text{-}^{21}\) with a central theme of resolving structural details. The highly branched (often one grafted side-chain per backbone repeating unit) structure of these macromolecules generates enough steric repulsion between side-chains to result in a highly extended, cylindrical conformation. Bottlebrush polymers prepared by the “grafting-through” or “macromonomer” method typically range in size from 10 – 100 nm and thus their structures in solution are best resolved by small-angle scattering techniques.

In our previous study, we focused on small-angle neutron scattering (SANS) results from bottlebrush polymers with polystyrene (PS) side chains prepared via the “grafting-through” method\(^14\). Poly(norbornene)-graft-PS (PNb-g-PS) bottlebrushes had side-chain lengths (\(N_{SC}\)) from 14 – 54 and backbone lengths (\(N_{BB}\)) from 10 – 264. We measured a shape transition from spherical to elongated bottlebrush polymers when the backbone degree of polymerization (DP) is sufficiently long (DP > 120)\(^14\). Bottlebrush polymers undergo a shape transformation when the backbone length becomes longer than twice the side-chain length, which forces the backbone to become highly stretched to accommodate increased side-chain packing\(^14\text{-}^{17}\text{-}^{22}\). A limitation of this study is that the bottlebrush
series varied in side-chain and backbone length simultaneously. Here we report a well-defined series of bottlebrush polymers with poly(lactic acid) (PLA) side-chains with systematic variations in side-chain and backbone lengths prepared by “grafting-through”.

Structural details of PLA grafted bottlebrush materials have recently been studied by combining SANS experimental data with coarse-grain molecular dynamics (CG-MD) simulations. Ahn, et al. studied the evolution of macromolecular size of PNb-g-PLA bottlebrushes as a function of macromonomer conversion (or backbone length) by size exclusion chromatography (SEC) and SANS and compared results to CG-MS simulations. They found a change in bottlebrush shape from globular to elongated particle as the backbone DP and conversion increased. The PLA bottlebrushes studied by Ahn and coworkers have short side-chains \( N_{SC} = 20; M_n = 1570 \text{ g mol}^{-1} \) and backbone lengths from \( N_{BB} = 16 \) to 483. The contour length from fitting a flexible cylinder model results in a sharp increase for bottlebrushes with \( N_{BB} > 100 \), in strong agreement with our previous findings. The samples presented in their study have varying amounts of linear macromonomer present, which required additional fitting parameters. Fitted Kuhn lengths measured 132 – 217 Å for \( N_{BB} > 100 \) and 36 – 211 Å for \( 16 < N_{BB} < 73 \). Zhang, et al. studied the side-chain relaxation of the same PNb-g-PLA materials with variations in \( N_{SC} \) (5, 10, or 19) and constant \( N_{BB} = 25 \). These PLA grafted materials are in the spherical regime and their simulations predict a strong dependence on side-chain conformation with solvent quality. Zhang concludes that rigid cylinder or ellipsoidal form factors, rather than a flexible cylinder, may be more appropriate for bottlebrush polymers with similar \( N_{BB} \) values (ie. in the spherical regime). Pesek, et al. and others demonstrated that a flexible cylinder model is appropriate for larger \( N_{BB} \).

In this study, we focus on five bottlebrush polymers with \( N_{SC} = 34 \) and four bottlebrush polymers with \( N_{SC} = 57 \) with systematic variations in backbone length, \( N_{BB} \), ranging from 25 - 215. Poly(norbornene)-graft-Poly(lactic acid) (PNb-g-PLA) bottlebrushes are prepared by “grafting-through” of linear macromonomers by polymerizing terminal norbornene units by ring opening metathesis polymerization (ROMP). Detailed characterization of the bottlebrush polymers by light scattering, \(^1\)H NMR, and gel permeation chromatography (GPC) provide structural information that is applied to
small-angle neutron scattering (SANS) data to extrapolate the dependence of molecular conformation on \(N_{SC}\) and \(N_{BB}\). The glass transition temperature, \(T_g\), of the bottlebrush series is also reported.

3.2 Results and Discussion

3.2.1 PNb-g-PLA bottlebrush synthesis

PNb-g-PLA bottlebrush polymers were prepared by ROMP polymerization of norbornene terminated PLA macromonomers (Scheme 3.1). Side-chain PLA macromonomers were prepared by ring-opening polymerization and have molecular weights of 2 600 and 4 300 g mol\(^{-1}\) which corresponds to \(N_{SC}\) values of 34 and 57, respectively. PNb\(_{25}\)-g-PLA\(_{34}\) and PNb\(_{39}\)-g-PLA\(_{57}\) were prepared using NB-PLA macromonomers with slightly different (less than 5% variance) side-chain molecular weights than those in the series. The precise molecular weights and \(N_{SC}\) values are reported in Table 3.1, but we use the series values of \(N_{SC}\) 34 and 57 for clarity. PNb-g-PLA bottlebrushes with \(N_{SC}=34\) have molecular weights (\(M_w\)) 64.6 – 463 kg mol\(^{-1}\), PDI less than 1.1 and macromonomer conversions greater than 90 %. PNb-g-PLA bottlebrushes with \(N_{SC}=57\) have \(M_w\) 172 – 969 kg mol\(^{-1}\), PDI less than 1.22 and macromonomer conversions greater than 95 %. Due to extremely high reactivity and fast kinetics\(^{23}\) of NB-PLA macromonomer, the synthesis of a well-defined series of bottlebrush polymers with systematically increasing backbone lengths was feasible, as shown in Figure 3.1. NMR confirmed nearly 100% monomer conversion in all cases.

![Scheme 3.1: Two-step synthesis of Nb-PLAM macromonomers by ROP and bottlebrush polymers by ROMP.](image-url)
Table 3.1: Properties of PNb-g-PLA bottlebrush polymers with $N_{SC} = 34$ and 57 and systematic variations in $N_{BB}$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{H,SC}$ (g/mol)</th>
<th>$N_{SC}$</th>
<th>[MM]/cat.</th>
<th>$N_{BB}$</th>
<th>$M_{w,BB}$ (g/mol)</th>
<th>PDI ($M_w/M_n$)</th>
<th>% MM conv.</th>
<th>$dn/dc$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb_{25}-g-PLA_{34}</td>
<td>2630</td>
<td>33</td>
<td>25</td>
<td>25</td>
<td>64 600</td>
<td>1.06</td>
<td>90</td>
<td>0.051</td>
</tr>
<tr>
<td>PNb_{52}-g-PLA_{34}</td>
<td>2680</td>
<td>34</td>
<td>50</td>
<td>52</td>
<td>138 000</td>
<td>1.10</td>
<td>98</td>
<td>0.056</td>
</tr>
<tr>
<td>PNb_{89}-g-PLA_{34}</td>
<td>2680</td>
<td>34</td>
<td>100</td>
<td>89</td>
<td>234 000</td>
<td>1.09</td>
<td>99</td>
<td>0.052</td>
</tr>
<tr>
<td>PNb_{144}-g-PLA_{34}</td>
<td>2680</td>
<td>34</td>
<td>150</td>
<td>144</td>
<td>386 000</td>
<td>1.11</td>
<td>100</td>
<td>0.051</td>
</tr>
<tr>
<td>PNb_{174}-g-PLA_{34}</td>
<td>2680</td>
<td>34</td>
<td>200</td>
<td>174</td>
<td>463 000</td>
<td>1.11</td>
<td>99</td>
<td>0.050</td>
</tr>
<tr>
<td>PNb_{39}-g-PLA_{57}</td>
<td>4550</td>
<td>60</td>
<td>50</td>
<td>39</td>
<td>172 000</td>
<td>1.22</td>
<td>95</td>
<td>0.049</td>
</tr>
<tr>
<td>PNb_{94}-g-PLA_{57}</td>
<td>4360</td>
<td>57</td>
<td>100</td>
<td>94</td>
<td>421 000</td>
<td>1.11</td>
<td>99</td>
<td>0.045</td>
</tr>
<tr>
<td>PNb_{143}-g-PLA_{57}</td>
<td>4360</td>
<td>57</td>
<td>150</td>
<td>143</td>
<td>643 000</td>
<td>1.13</td>
<td>99</td>
<td>0.046</td>
</tr>
<tr>
<td>PNb_{215}-g-PLA_{57}</td>
<td>4360</td>
<td>57</td>
<td>200</td>
<td>215</td>
<td>969 000</td>
<td>1.14</td>
<td>99</td>
<td>0.042</td>
</tr>
</tbody>
</table>
3.2. Small-Angle Neutron Scattering

Bottlebrush polymers made by “grafting-through” have a constant radial length throughout the polymer because each backbone repeating unit is guaranteed to have a grafted side-chain polymer of equal molecular weight. Small-angle neutron scattering (SANS) experiments provide quantitative determination of bottlebrush shape (form factor) and sub-nanometer features in the internal structures of the material. SANS experiments were performed by dissolving PNB-g-PLA bottlebrushes at 1 wt% in 1,4-dioxane-d8 or toluene-d8. The Hansen solubility parameter of PLA in dioxane is 20.5 and PLA chains are predicted to be soluble\(^{24}\). The Hansen solubility parameter for toluene is 18.2 and PLA chains should be strongly swollen\(^{24}\). SANS data for PNB-g-PLA\(_{34}\) and PNB-g-PLA\(_{57}\) in 1,4-dioxane-d8 are shown in Figure 3.2. SANS data for PNB-g-PLA\(_{34}\) in toluene-d8 are shown in Figure 3.3. Similar to our previous report\(^{14}\), we first apply an empirical model for arbitrary shapes, the Guinier-Porod model\(^{25}\), followed by a rigid and flexible cylindrical model, where appropriate, using IGOR-PRO software\(^{26}\).
Figure 3.2: SANS traces for PLA bottlebrush series in 1,4-dioxane-d8. Bottlebrush polymers with \( N_{SC} = 34 \) and systematic variations in \( N_{SBB} \) are shown in the top figure. Bottlebrush polymers with \( N_{SC} = 57 \) and systematic variations in \( N_{SBB} \) are shown in the bottom figure.

SANS data can be qualitatively interpreted by focusing on three key regions: low \( q \) (\( q < 0.01 \)), middle-\( q \) (\( 0.01 < q < 0.1 \)) and high-\( q \) (\( q > 0.1 \)). A detailed explanation of interpreting SANS data for densely grafted bottlebrush polymers can be found in our previous report \(^{14} \) (Chapter 1) and a brief account is included here. Scattering at low-\( q \) correlated to features representative of the entire bottlebrush molecule (such as total bottlebrush size, \( >10 \) nm) and an upturn in low-\( q \) typically indicates intermolecular aggregation. The middle-\( q \) region provides information about bottlebrush polymers...
cross-section or radial distance. A qualitative description of the SANS data reported here is discussed below.

PNb-g-PLA bottlebrushes in 1,4-dioxane-$d_8$ are shown in Figure 3.2. For bottlebrush polymers with the same side-chain molecular weights, the scatter profiles for the series overlap strongly in the middle-$q$ region, indicating that they have nearly identical cross-sectional areas (ie. same side-chain extension). The middle-$q$ region ($0.009 < q < 0.03$) displays a more pronounced difference in the molecular sizes as seen by an increased scattered intensity as the backbone length increases. All bottlebrush polymers measured have some degree of aggregation in solution, as evident by the low-$q$ upturn ($q < 0.009$).

![Graph showing SANS traces for PNb-g-PLA (N_SC = 34) bottlebrush series in toluene-$d_8$.](image)

**Figure 3.3:** SANS traces for PNb-g-PLA ($N_{SC} = 34$) bottlebrush series in toluene-$d_8$.

PNb-g-PLA bottlebrushes in toluene-$d_8$ (Figure 3.3) have sufficient amount of aggregation such that it interferes with the plateau region at middle to low-$q$. The scatter profiles for all polymers in this series overlap strongly in the middle-$q$ region, indicating that they have nearly identical cross-sectional areas (ie. same side-chain extension). In the $0.009 < q < 0.03$ regime we see that as the backbone DP ($N_{BB}$) increases from 50 to 200 the intensity increases which confirms a larger molecular size. Due to aggregation interfering with the slope in middle-$q$, we were unable to further analyze bottlebrush conformation by fitting with theoretical models.
We measured the solution conformation of single-particle bottlebrush polymers with systematic variations in $N_{SC}$ and $N_{BB}$ in dioxane by analysis with the Guinier-Porod model\textsuperscript{25}. Results for the Guinier-Porod model are presented in Table 3.2 and Figure 3.4. For bottlebrushes with $N_{SC} = 34$, the Guinier-Porod model predicts the radius of gyration, $R_g$, between 38.1 and 50.4 Å, while for $N_{SC} = 57$ the $R_g$ is 53.4 to 60.4 Å (Table 3.2). It should be noted, however, that for spherical particles ($N_{BB} \leq 100$) the value for $R_g$ does not represent the radial cross-section but rather the $R_g$ for the whole particle. The dimension parameter increases with $N_{BB}$ as expected. The bottlebrushes transition from a spherical shape ($s \sim 0$) to more elongated cylinders ($s \sim 0.6$) as the backbone length extends beyond the length of the particle diameter ($2 \times R$).

**Table 3.2:** Fitted results for Guinier-Porod model of PNd-g-PLA bottlebrush SANS data in 1,4 dioxane-$d_8$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$S$</th>
<th>$R_g$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNd$<em>{25}$-g-PLA$</em>{34}$</td>
<td>0.0 *</td>
<td>41.1 ± 0.07</td>
<td>3.5 ± 0.02</td>
</tr>
<tr>
<td>PNd$<em>{52}$-g-PLA$</em>{34}$</td>
<td>0.03 ± 0.02</td>
<td>50.4 ± 0.47</td>
<td>3.0 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{89}$-g-PLA$</em>{34}$</td>
<td>0.29 ± 0.02</td>
<td>48.0 ± 0.39</td>
<td>3.1 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{144}$-g-PLA$</em>{34}$</td>
<td>0.69 ± 0.01</td>
<td>38.1 ± 0.35</td>
<td>3.0 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{174}$-g-PLA$</em>{34}$</td>
<td>0.60 ± 0.01</td>
<td>40.6 ± 0.36</td>
<td>3.1 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{39}$-g-PLA$</em>{57}$</td>
<td>0.0 *</td>
<td>59.8 ± 0.10</td>
<td>3.5 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{94}$-g-PLA$</em>{57}$</td>
<td>0.38 ± 0.02</td>
<td>60.4 ± 0.75</td>
<td>3.1 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{143}$-g-PLA$</em>{57}$</td>
<td>0.51 ± 0.02</td>
<td>56.6 ± 0.65</td>
<td>3.2 ± 0.01</td>
</tr>
<tr>
<td>PNd$<em>{215}$-g-PLA$</em>{57}$</td>
<td>0.63 ± 0.02</td>
<td>53.4 ± 0.63</td>
<td>3.3 ± 0.01</td>
</tr>
</tbody>
</table>

* For these samples, $S$ was defined as 0.0 when fitting because fitted values were < 0 and had no physical interpretation.
Next we fit PNb-g-PLA bottlebrush polymers SANS results from 1,4-dioxane-d8 to a rigid cylinder model. This model is more appropriate for smaller bottlebrush polymers (total molecular length less than the Kuhn length)\textsuperscript{16}, but results from all materials provide data on trends in the bottlebrush samples. Fitted results are shown in Table 3.3. Fitted lengths ($L_C$) increase predictably with $N_{BB}$ for both side-chain molecular weights. Estimated particle lengths from rigid cylinder model are 2.8 – 25.6 nm for $N_{SC} = 34$ and 15.5 – 37.9 nm for $N_{SC} = 57$. Fitted radii, $R_C$, are consistent throughout each side-chain series. For $N_{SC} = 34$ the average $R_C$ is 46.4 ± 1.3 Å and for $N_{SC} = 57$ the average $R_C$ is slightly larger at 59.8 ± 3.7 Å.

For elongated bottlebrush polymers, applying a flexible cylinder model to SANS data is more appropriate\textsuperscript{2,14,17,18}. Flexible cylinders are described by a contour length ($CL_F$), a Kuhn step length ($\lambda_K$), and a radius ($R_F$). Results for the Guinier-Porod model are presented in Table 3.3 and Figure 3.4. In analyzing SANS data by the flexible cylinder model, the fitted values for the Kuhn length were physically unrealistic and inconsistent. Therefore we defined the Kuhn length, $\lambda_K$, to be 168 Å based on previously reported values\textsuperscript{2,14,15,27}. Ahn and coworkers reported the Kuhn length for very similar PNb-g-PLA bottlebrushes to have $\lambda_K$ 132 – 217 Å\textsuperscript{15}. Kawaguchi et al\textsuperscript{27} determined the persistence length of 168 Å for polystyrene-\textit{graft}-poly(ethylene glycol) polymers by multi-angle laser light scattering-size exclusion chromatography fit to the worm-like chain model. Rathgeber et al\textsuperscript{2} predicted the persistence length of poly(hydroxyethyl methacrylate)-\textit{graft}-poly(n-butyl acrylate) system to be 350 ± 20 Å. Based on these results we assign $\lambda_K$ value of 168 Å when fitting a flexible cylinder model. Fitted contour lengths, $CL_F$, of bottlebrush polymers increase with increasing $N_{BB}$. Polymers are 92.2 – 419 Å long, and $CL_F$ values are typically 10 – 30 % larger than $L_C$ by fitting with a rigid cylinder. However some $CL_F$ values are smaller than $L_C$. Radii from the flexible cylinder model slightly smaller than $R_C$ and are overall in good agreement with results from cylinder model.
Figure 3.4 Results from the Guinier-Porod (A, B) and Flexible Cylinder (C,D) models. Radii are roughly constant for each side-chain molecular weight by Guinier-Porod (A) and flexible cylinder (C) analysis. Dimension parameter, $s$, increases with backbone length (B) and contour length results increase with backbone length, $N_{BB}$, as expected (D).
Table 3.3: Fitted results for cylinder and flexible cylinder models from PNb-g-PLA bottlebrush SANS data in 1,4 dioxane-d8.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cylinder Model</th>
<th>Flexible Cylinder Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_C$</td>
<td>$R_C$</td>
</tr>
<tr>
<td>PNb$<em>{25}$-g-PLA$</em>{34}$</td>
<td>78 ± 29.7</td>
<td>47.3 ± 8.1</td>
</tr>
<tr>
<td>PNb$<em>{52}$-g-PLA$</em>{34}$</td>
<td>149 ± 1.1</td>
<td>44.2 ± 0.2</td>
</tr>
<tr>
<td>PNb$<em>{89}$-g-PLA$</em>{34}$</td>
<td>197 ± 1.5</td>
<td>47.2 ± 0.2</td>
</tr>
<tr>
<td>PNb$<em>{144}$-g-PLA$</em>{34}$</td>
<td>269 ± 3.7</td>
<td>46.4 ± 0.2</td>
</tr>
<tr>
<td>PNb$<em>{174}$-g-PLA$</em>{34}$</td>
<td>256 ± 2.9</td>
<td>47.3 ± 0.2</td>
</tr>
<tr>
<td>PNb$<em>{39}$-g-PLA$</em>{57}$</td>
<td>155 ± 1.1</td>
<td>54.2 ± 0.2</td>
</tr>
<tr>
<td>PNb$<em>{94}$-g-PLA$</em>{57}$</td>
<td>259 ± 2.9</td>
<td>61.8 ± 0.3</td>
</tr>
<tr>
<td>PNb$<em>{143}$-g-PLA$</em>{57}$</td>
<td>292 ± 3.7</td>
<td>61.5 ± 0.3</td>
</tr>
<tr>
<td>PNb$<em>{215}$-g-PLA$</em>{57}$</td>
<td>379 ± 8.3</td>
<td>61.7 ± 0.3</td>
</tr>
</tbody>
</table>

Lastly, we can analyze the side-chain and backbone polymer chain extension by applying a power-law scaling to the polymer radii and length fitted values by the equations:

\[
Polymer\ Radius = R_F = l_L \times N_{SC}^{v_{SC}} \quad \text{(Eqn 3.1)}
\]

\[
Polymer\ Length = CL_F = l_N \times N_{BB}^{v_{BB}} \quad \text{(Eqn 3.2)}
\]

Where polymer radius, $R_F$, and contour length, $CL_F$, (taken from flexible cylinder results), $l_L$ is length of repeating unit of poly(lactic acid) side-chains, $l_N$ is length of poly(norbornene) repeating unit, and $v_{SC}$ and $v_{BB}$ are the resulting chain extension parameters for side-chain and backbone, respectively. We estimate the atomic bond lengths of the atoms in repeating units of poly(lactic acid) ($l_L$) and poly(norbornene) ($l_N$)
to be 5.82 Å and 7.34 Å, respectively\textsuperscript{28}. Using this relation, we find that the side-chains extension scales as $v_{SC} = 0.56 \pm 0.017$ for $N_{SC} = 34$ and $v_{SC} = 0.55 \pm 0.004$ for $N_{SC} = 57$. The side-chain extension is not statistically different for different side-chain molecular weights and is more extended than free polymers in solution. The backbone poly(norbornene) polymers are more extended with longer side-chain polymers. For $N_{SC} = 57$, $v_{BB}$ is found to be $0.80 \pm 0.04$, while for shorter side-chains $N_{SC} = 34$ we report $v_{BB}$ value of $0.75 \pm 0.02$.

Table 3.4: Chain extension analysis for PNb-g- in 1,4 dioxane-$d8$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$v_{SC}$</th>
<th>$v_{BB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb\textsubscript{25}-g-PLA\textsubscript{34}</td>
<td>0.54</td>
<td>0.77</td>
</tr>
<tr>
<td>PNb\textsubscript{52}-g-PLA\textsubscript{34}</td>
<td>0.58</td>
<td>0.75</td>
</tr>
<tr>
<td>PNb\textsubscript{89}-g-PLA\textsubscript{34}</td>
<td>0.57</td>
<td>0.76</td>
</tr>
<tr>
<td>PNb\textsubscript{144}-g-PLA\textsubscript{34}</td>
<td>0.56</td>
<td>0.75</td>
</tr>
<tr>
<td>PNb\textsubscript{174}-g-PLA\textsubscript{34}</td>
<td>0.56</td>
<td>0.72</td>
</tr>
<tr>
<td>PNb\textsubscript{39}-g-PLA\textsubscript{57}</td>
<td>0.56</td>
<td>0.79</td>
</tr>
<tr>
<td>PNb\textsubscript{94}-g-PLA\textsubscript{57}</td>
<td>0.55</td>
<td>0.85</td>
</tr>
<tr>
<td>PNb\textsubscript{143}-g-PLA\textsubscript{57}</td>
<td>0.55</td>
<td>0.79</td>
</tr>
<tr>
<td>PNb\textsubscript{215}-g-PLA\textsubscript{57}</td>
<td>0.55</td>
<td>0.73</td>
</tr>
</tbody>
</table>

3.2.3. Size analysis by TEM and DLS.

Bottlebrush polymer size from SANS is compared to TEM micrographs (dried polymer) and DLS size distributions (5 mg/mL organic solvent, THF). Select PNb-g-PLA bottlebrush polymers were analyzed by TEM prepared by drop-casting dilute solutions.
onto gold TEM grids and negatively stained with PtO$_4$ (polymers appear white in a dark background). TEM images are shown in Figure 3.5. PNb$_{52}$-g-PLA$_{34}$ is 16.5 ± 4 nm and appears mostly spherical. PNb$_{174}$-g-PLA$_{34}$ has the same $N_{SC}$ but longer backbone and TEM confirms the larger size with an average size of 19.6 ± 3 nm. For polymers with $N_{SC} = 57$, the shorted backbone length $N_{BB} = 39$ is 18.3 ± 4 nm whereas polymers with $N_{BB} = 215$ are 19.7 ± 3 nm. Due to sample preparation techniques, bottlebrush polymers observed by TEM are dried onto a flat surface and therefore may not reflect an accurate size estimate of bottlebrush polymers in solution. Trends observed by TEM are consistent with those observed by SANS and those expected based on changes in structural parameters.

**Figure 3.5:** TEM micrographs of bottlebrush polymers with PLA side-chains. A) PLA$_{34-50}$; B) PLA$_{34-200}$; C) PLA$_{46-50}$; D) PLA$_{34-200}$.

Dynamic light scattering (DLS) of PNb-g-PLA bottlebrush polymers were carried out at 1 wt% THF. The number average diameters are reported in Table 3.5 and DLS size distributions are shown in Figure 3.6. Polymers with $N_{SC} = 34$ were difficult to measure due to large number of aggregates. The measured diameter of bottlebrush polymers with $N_{SC} = 57$ increases with backbone DP from 22.8 nm to 27.6 nm in THF.
Figure 3.6: DLS number distributions for bottlebrush polymers ($N_{BB} = 57$) in THF.  A) PNb$_{39}$-g-PLA$_{57}$, B) PNb$_{94}$-g-PLA$_{57}$, C) PNb$_{143}$-g-PLA$_{57}$, and D) PNb$_{215}$-g-PLA$_{57}$.
Table 3.5: Summary of PNb-g-PLA thermal properties ($T_g$) and size estimates from DLS, TEM, and SANS.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>DLS (D, nm)</th>
<th>TEM (D, nm)</th>
<th>SANS (D, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb52-g-PLA34</td>
<td>49.2</td>
<td>20.6</td>
<td>16.5 ± 4</td>
<td>14.1 ± 0.2</td>
</tr>
<tr>
<td>PNb89-g-PLA34</td>
<td>50.0</td>
<td>22.8</td>
<td>*</td>
<td>21.9 ± 0.3</td>
</tr>
<tr>
<td>PNb144-g-PLA34</td>
<td>50.4</td>
<td>*</td>
<td>*</td>
<td>30.9 ± 0.4</td>
</tr>
<tr>
<td>PNb174-g-PLA34</td>
<td>50.2</td>
<td>*</td>
<td>19.6 ± 3</td>
<td>29.7 ± 0.3</td>
</tr>
<tr>
<td>PNb39-g-PLA57</td>
<td>51.4</td>
<td>22.8</td>
<td>18.3 ± 4</td>
<td>13.2 ± 0.2</td>
</tr>
<tr>
<td>PNb94-g-PLA57</td>
<td>49.7</td>
<td>25.2</td>
<td>*</td>
<td>34.2 ± 0.6</td>
</tr>
<tr>
<td>PNb143-g-PLA57</td>
<td>51.0</td>
<td>25.2</td>
<td>*</td>
<td>37.8 ± 0.5</td>
</tr>
<tr>
<td>PNb215-g-PLA57</td>
<td>50.5</td>
<td>27.6</td>
<td>19.7 ± 3</td>
<td>41.9 ± 0.6</td>
</tr>
</tbody>
</table>

* Data unavailable.

3.2.4. Bottlebrush Thermal Properties

Glass transition temperatures ($T_g$) of bottlebrush polymers series were determined by DSC experiments. The thermal properties of highly branched bottlebrush polymers have been reported in a limited number of studies\textsuperscript{29}. The $T_g$ of linear polymer chains is known to increase logarithmically with increasing molecular weight according to the Flory-Fox equation ($T_g = T_{g*} - K/M_n$). Results from DSC experiments are presented in Table 3.5 and shown graphically in Figure 3.7. We find that the $T_g$ of bottlebrush polymers with $N_{SC} = 34$ does not increase with large molecular weight (backbone length) as expected. For bottlebrush polymers with $N_{SC} = 34$ and $N_{SC} = 57$ the average $T_g = 50.0 \pm 0.5$ °C and $T_g = 50.7 \pm 0.7$ °C, respectively. From these results, we conclude that the side-chain molecular weight and overall molecular weight do not affect the thermal properties of bottlebrush polymers above molecular weight 138 000 g mol\textsuperscript{-1}. 

58
Figure 3.7 Glass transition temperature, \( T_g \), of PNb-g-PLA bottlebrush polymers determined by DSC. The \( T_g \) has a nearly constant value of 50.3 ± 0.7 °C.

3.3 Conclusion

PNb-g-PLA bottlebrush polymers with side-chain lengths \( N_{SC} = 34 \) and \( N_{SC} = 57 \) and systematic variations in \( N_{BB} = 25 \) - 215 were prepared by ROMP polymerization of norbornene terminated PLA macromonomers. The resulting bottlebrush series have molecular weights 64.6 – 969 kg mol\(^{-1}\), PDI less than 1.22, and macromonomer conversions over 90%. PNb-g-PLA bottlebrushes were dissolved in 1,4-dioxane-d8 or toluene-d8 and analyzed by applying Guinier-Porod model, rigid cylinder and flexible cylindrical model to SANS experimental data. For bottlebrushes with \( N_{SC} = 34 \), the Guinier-Porod model predicts the radius of gyration, \( R_g \), between 38.1 and 50.4 Å, while for \( N_{SC} = 57 \) the \( R_g \) is 53.4 to 60.4 Å. Estimated particle lengths from rigid cylinder model are 2.8 – 25.6 nm for \( N_{SC} = 34 \) and 15.5 – 37.9 nm for \( N_{SC} = 57 \). Bottlebrush polymer radii increase with side-chain length. The average fitted radii by the cylinder model for \( N_{SC} = 34 \) is 46.4 ± 1.3 Å and for \( N_{SC} = 57 \) the average \( R_C \) is slightly larger at 59.8 ± 3.7 Å. Polymer contour lengths from the flexible cylinder model are 92.2 – 419 Å, and \( CL_F \) values are typically 10 – 30 % larger than \( L_C \) by fitting with a rigid cylinder. By
fittings the results for polymer radius with a power-law model, we find the side-chain conformation scales with side-chain polymer length as \( \nu_{SC} = 0.56 \pm 0.013 \), which is consistent with a 3D- self avoiding walk (3D-SAW). TEM and DLS results from select bottlebrush polymers are in agreement with predicted size results from SANS data. The average glass transition temperature of PNb-g-PLA bottlebrushes polymers is 50.3 ± 0.7 °C., which is found to be independent of bottlebrush structural parameters \( N_{SC} \) and \( N_{BB} \).

3.4 Experimental

3.3.1 Materials

Lactide was purchased from Sigma-Aldrich and recrystallized from ethyl acetate twice prior to use. Norbornenyl alcohol was modified from a previous report\textsuperscript{23}. Anhydrous dichloromethane (DCM) was purchased from Sigma-Aldrich and degassed prior to use. Modified Grubb’s catalyst ((H\textsubscript{2}I\textsubscript{Mes})(pyr)\textsubscript{2}(Cl)\textsubscript{2}RuCHPh) was synthesized as previously described\textsuperscript{30}.

**Synthesis of norbornene-poly(D,L-Lactic acid) (NB-PLA).** NB-PLA\textsubscript{N} was synthesized via ring opening polymerization in the presence of stannous octoate and a norbornenyl-alcohol, modified from a previous report\textsuperscript{23}. In a representative reaction lactide (32.6 mmol, 4.7 g), N-(Hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide (Nb-OH) (2.33 mmol, 580.8 mg) and stannous octoate (0.17 mmol, 20 mg) reacted for 3.5 hours at 120°C. The polymer was collected by precipitation in methanol to yield NbPLA\textsubscript{34} (\( M_n 2678 \text{ g mol}^{-1} \ PDI 1.41 \), \textit{yield} ref QX38). The molecular weight of NbPLAM is varied by increasing the monomer feed ratio. NbPLA\textsubscript{46} (\( M_n 4700 \text{ g mol}^{-1} \ PDI 1.28 \), \textit{yield} )

**Synthesis of Poly(norbornene)-graft-poly(lactic acid) bottlebrush polymers (PNb-g-PLA).** Subsequent ring-opening metathesis polymerization (ROMP) of the terminal norbornene afforded bottlebrush polymers with polynorbornene backbones and PLA side-chains. Slightly modified from our previous report\textsuperscript{14}, macromonomer NbPLAM (0.1 g, ___mmol) was added to a 5mL round bottom flask equipped with a stir bar. The flask was vacuum dried and backfilled with nitrogen three times, followed by the addition
of DCM (0.05 M). A stock solution of Grubb’s catalyst (0.01 g in 1.0 mL DCM) was added to the macromonomer solution at specified molar ratios. Kinetics analysis of ROMP polymerization shows that at t = 5 minutes, more than 95% of macromonomer consumption is achieved. After two hours, the reaction is quenched by addition of butyl vinyl ether (0.1 mL) followed by precipitation in 100 mL cold methanol.

3.3.2 Instrumentation

**Gel-Permeation Chromatography (GPC).** Polymer molecular weights and molecular weight polydispersities (PDIs) were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10 000 Å pore sizes), an Agilent variable-wavelength UV/vis detector, a Wyatt technology HELEOS II multiangle laser light scattering (MALLS) detector (λ = 658 nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/vis (SEC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer dn/dc values were calculated by assuming 100% mass recovery.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Proton NMR (¹H NMR) spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm o.d. tubes with a concentration of 10 mg/mL.

**Small-Angle Neutron Scattering (SANS).** SANS measurements were performed at the National Institute of Standards and Technology Center for Neutron Research on the NG3 and NG7 30 m instruments with a neutron wavelength of λ = 6 Å. For measurements in dioxane, three sample–detector distances were used (1.3, 4, and 15 m), providing an overall q range of 0.0014 Å⁻¹ < q < 0.4 Å⁻¹. For measurements in toluene, three sample–detector distances were used (1.3, 4, and 13 m), providing an overall q range of 0.003 Å⁻¹ < q < 0.4 Å⁻¹. Polymer samples were prepared at a mass fraction of 1% in deuterated solvent and allowed to equilibrate at RT for at least 4 h. Temperature control was provided by a water circulation bath, and was held constant at T = 25° C. Scattering data
were corrected for the solvent baseline with a scale factor (0.95–1.02) appropriate for the mass fraction of solvent. Model fitting was performed using NCNR Data Analysis IGOR PRO software 26 and the Guinier–Porod,25 cylinder,31 and flexible cylinder32,33 models.

**Transmission Electron Microscopy (TEM).** TEM was performed on JEOL 2010 TEM. Polymer solutions (0.1–1 mg/mL polymer in chloroform) were drop-cast onto carbon grids, dried, and stained with 10% phosphotungstic acid (PTA) and immediately transferred to the microscope for imaging.

**Dynamic Light Scattering (DLS).** DLS measurements were performed on a Malvern Zen 3600 Zetasizer (Zetasizer Nano) operating in size mode. Polymer solutions were prepared at 5 - 10 mg/mL in THF and filtered prior to measurement.

**Differential Scanning Calorimetry (DSC).** DSC measurements were performed on TA Instruments DSC Q20 series. Polymer samples (2 – 5 mg) were placed in hermetically sealed aluminum DSC pans purchased from Thermal Support. Samples were cooled to -40 °C for 30 minutes. Each cycle consisted of samples heated to 200 °C at 5 °C/minute, held isothermally for 5 minutes, then cooled to -40 °C. A total of three cycles were run per sample and Tg values were taken from the second cycle.

### 3.5 References


4. Synthesis of bottlebrush copolymers based on poly(dimethylsiloxane) for surface active additives

[Portions of the work described in this chapter have been submitted for publication: Stacy L. Pesek, Yen-Hao Lin, Will Kasper, Rafael Verduzco, et al, “Synthesis of bottlebrush copolymers based on poly(dimethylsiloxane) for surface active additives” 2015 and portions of this work have been published: Indranil Mitra, Xianyu Li, Stacy L. Pesek, Boris Makarenko, Brad S. Lokitz, David Uhrig, John F. Anker, Rafael Verduzco, and Gila Stein “Thin Film Phase Behavior of Bottlebrush/Linear Polymer Blends” Macromolecules, 2014, 47, 5269 - 5276.]

4.1 Abstract

Bottlebrush polymers have been used as surface-active additives for chemically-identical linear polymers because they spontaneously accumulate at surfaces through an entropy-mediated process. In this work, we introduce enthalpic contributions by designing bottlebrush polymer additives with mixed side-chain chemistries. Bottlebrush polymers with poly(dimethylsiloxane) (PDMS) side-chains and bottlebrush copolymers with PDMS and poly(lactic acid) (PLA) side-chains are synthesized using ring opening metathesis polymerization, which produces branched PDMS polymers and copolymers with a higher grafting density and longer side-chains compared with previously reported techniques. Blend films of PDMS/PLA bottlebrush copolymers in a linear PLA matrix are characterized by water contact angle, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and optical microscopy measurements. The bottlebrush copolymers spontaneously segregate to the top surface, as demonstrated by increased
hydrophobicity, a significant surface excess of silicon, and an absence of lateral phase separation in atomic force microscopy (AFM) and optical microscopy measurements. Significantly, the bottlebrush copolymer additives exhibit rapid surface segregation during film casting, and the addition of a second side-chain chemistry can deliver unique surface functions.

4.2 Introduction

Bottlebrush polymers have unique properties stemming from their highly branched architecture. The properties and target applications of bottlebrushes are primarily determined by the composition of the side-chain polymers, as they shield the backbone and are generally flexible and able to interact with their environment. Bottlebrush polymer macromolecules range in size from tens to hundreds of nanometers, may be spherical or elongated in shape, and can be designed for applications including stimuli responsive films, nanolithography, drug delivery, and lubricants, as discussed in a recent review.

Our first study focusing on blends of bottlebrush polymers and linear polymers found branched bottlebrush polymers segregate to the top and bottom interfaces (depleted from bulk matrix polymer) in polymer thin-films (Figure 4.1). The bottlebrush side-chain composition matched that of the linear polymer matrix, and therefore segregation was driven by entropic effects. Bottlebrush polymers with polystyrene (PS) side-chains ($M_n$ 6.4, $N_{SC}$ 61) were mixed with linear deuterated PS ($M_n$ 2.0 – 254.9 kg mol$^{-1}$, length of matrix polymer $N_m$ = 19 - 2500) in a 1:9 vol/vol ratio and spun cast from toluene to form ~100 nm thin polymer films. Depth profiling of bottlebrush blends was characterized by secondary-ion mass spectroscopy (SIMS) in films as cast and after thermal annealing (2 and 7 days) and are shown in Figure 4.2. These nearly athermal systems exhibit wetting and dewetting transitions that drive bottlebrush dispersion or aggregation, respectively, and these effects depend on the relative degrees of polymerization of matrix chains $N_m$ to those of bottlebrush side-chains $N_{SC}$. When $N_m/N_{SC}$ is low (≤1.6), the bottlebrushes are dispersed throughout the film thickness with a slight excess at the free surface and substrate interfaces. When $N_m/N_{SC}$ is high (≥8), the bottlebrushes are depleted from the interior of the film and strongly segregated at the
interfaces. The interfacial excess is driven by an entropic depletion attraction effect: larger branched molecules are adsorbed (attracted) to the interfaces, and the linear chains are displaced to the film’s interior where they gain conformational entropy. The bottlebrushes prefer to accumulate at the silicon substrate over the air interface, and this may be driven by the more restrictive condition of a hard boundary or weak van der Waals interactions with the underlying silicon. These studies demonstrate that low concentrations of certain bottlebrush polymer architectures can generate brushlike surfaces and interfaces in any thermoplastic material through a spontaneous, entropy-driven segregation process.

**Figure 4.1** Bottlebrush polymer blends with linear polymer of the same composition segregate to the top and bottom surface due to entropic depletion. Bottlebrush polymers segregate more strongly when the matrix polymer molecular weight is much higher than that of the bottlebrush side-chain ($N_m >> N_{SC}$).
Figure 4.2 Concentration of bottlebrush polymer (φ) as a function of depth into the film (depth 0 denotes the air interface, and 150 nm is the substrate interface). Each column features a different matrix chain length $N_m$, while each row shows a different annealing time (165 °C). Open symbols denote the SIMS data (red is $N_b = 193$, and blue is $N_b = 90$). Solid black and dashed green lines are fits to the model described in the discussion.

A potential application of bottlebrush polymers is as specialty additives to modify polymer film surface properties. Prior experimental$^{11-12}$ and computational studies$^{12-14}$ have demonstrated the surface segregation of branched polymers in blends with chemically identical linear polymers. The migration of linear copolymer additives, where the additive contained a compatibilizing (same composition as matrix polymer) and low-surface energy component, has also been reported.$^{15-16}$ Here, we explore blends of bottlebrush copolymers that contain two different types of side chains (see Figure 4.3). The use of bottlebrush copolymers with two different side-chains introduces enthalpic interactions$^{18}$ as a driving force for segregation, while simultaneously delivering a desired surface functionality.
**Figure 4.3** Schematic for the modification of polymer thin films through the addition of bottlebrush copolymers, which segregate to the film surface due to enthalpic and entropic effects.

We focus on bottlebrush polymers and copolymers with poly(dimethylsiloxane) (PDMS) side-chains. PDMS is an inorganic polymer with low surface energy (~ 20 mN/m) and low glass transition temperature ($T_g \sim -120^\circ$C). PDMS has been demonstrated for applications including anti-biofouling,\textsuperscript{19-24} directed self-assembly,\textsuperscript{25-26} nanolithography,\textsuperscript{3, 25-27} and gas separation membranes.\textsuperscript{28-29} There are limited reports on branched PDMS polymers.\textsuperscript{28-34} RAFT polymerization of methacrylate-terminated PDMS has produced bottlebrush PDMS with side-chain $M_n$ of 1 or 4.3 kg/mol and backbone degree of polymerizations (DP) up to 70 for the shorter side-chains.\textsuperscript{30-31} Masuda et al\textsuperscript{32} reported branched PDMS material with $M_w$ up to 349 kg/mol but with broad molecular weight dispersity ($\mathcal{D} = 1.7 – 3.2$). An approach based on ring-opening metathesis polymerization (ROMP) was limited to very short oligo-PDMS chains, with a maximum side-chain DP of 8.\textsuperscript{29}

Herein, we report the synthesis of bottlebrush polymers with PDMS side-chains and bottlebrush copolymers with PDMS and poly(lactic acid) (PLA) side-chains using a ROMP grafting-through synthesis approach and their use as surface-active additives. ROMP produces branched PDMS polymers and copolymers with a higher grafting density and longer side-chains compared with previous synthetic approaches. To investigate the segregation of PDMS/PLA bottlebrush copolymer additives in a linear PLA matrix, blend films are characterized by water contact angle (WCA), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and optical microscopy measurements. Our analysis shows that bottlebrush copolymers with mixed PDMS and PLA side-chains spontaneously segregate to the top surface, as demonstrated
by increased hydrophobicity, a significant excess of silicon at the top surface, and an absence of lateral phase separation in atomic force microscopy (AFM) and optical microscopy measurements. Bottlebrush copolymer additives are compared with diblock copolymer PLA-b-PDMS additives of a similar composition and with pure PDMS additives, and we find that bottlebrush copolymers segregate more strongly than diblock copolymers and produce more uniform films compared with PDMS homopolymer. This study shows that low concentrations of functional bottlebrush copolymer additives can introduce new surface properties in polymer films through a rapid and spontaneous demixing process.

4.3 Experimental
4.3.1 Materials
  Monoaminopropyl terminated polydimethylsiloxane - asymmetric ($M_w$ 2000 g mol$^{-1}$) (PDMS2k-NH$_2$) and monohydride terminated polydimethylsiloxane – asymmetric ($M_w$ 4500 - 5000 g mol$^{-1}$) (PDMS5k-SiH) were purchased from Gelest Inc. cis-5-Norbornene-exo-2,3-dicarboxylic anhydride (NB-OH), triethyl amine, dichloro (1,5-cyclooctadiene) platinum (II), and D, L-lactide were purchased from Sigma Aldrich. Modified Grubb’s catalyst ((H$_2$IMes)(pyr)$_2$(Cl)$_2$RuCHPh)$_3$ and N-(hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide$^2$ were prepared as previously reported. Lactide was recrystallized from ethyl acetate twice prior to use. All other reagents were used as received.

**Synthesis of 2k PDMS macromonomer, PDMS2k-NB.** PDMS2k-NH$_2$ (6.98 g, 3.21 mmol), triethyl amine (60 mg, 0.59 mmol), NB-OH (561.6 mg, 3.42 mmol) and 200 mL anhydrous toluene were added to a 250 mL round bottom flask equipped with a stir bar. The reaction flask was attached to a Dean-Stark trap with a condenser and allowed to react at 120 °C for 18 hours. The product was concentrated by rotary evaporation, and the final product isolated by silica gel chromatography with 9:1 hexanes:ethyl acetate as the eluent. PDMS2k-NB: $M_n$ 2815 g/mol (DP 35), $D$ 1.16, yield 1.4 g (26 % isolated yield).$^1$H NMR spectra of the final product is provided in the Supplemental Information Figure S4.1. $^1$H NMR. $\delta_H$ (400 MHz, CDCl$_3$): -0.8-0.2 (m, 310H, -O-Si-2(CH$_2$)-), 0.48 (m, 4H, Si-CH$_2$-CH$_2$), 0.79 (t, 3H, CH$_2$-CH$_3$), 1.18 (m, 2H, -CH$_2$-CH$_2$-CH$_3$), 1.25 (m,
2H, -CH₂-CH₂-CH₂-), 2.57 (s, 2H, CH-CH-CH₂-CH-), 3.2 (s, 2H, CH-CH-CH-C-), 3.35 (t, 2H, -N-CH₂-CH₂-), 6.2 (s, 2H, -CH-CH=CH-CH-).

**Synthesis of 5k PDMS macromonomer, PDMS5k-NB.** PDMS5k-SiH (5.36 g, 1.07 mmol) and allyl amine (1 mL, 1 g, 17.5 mmol) were added to a 100 mL round bottom flask with 5 mL anhydrous toluene, followed by addition of catalyst solution (5 mg dichloro (1,5-cyclooctadiene) platinum (II) in 2mL dichloromethane (DCM)). The reaction proceeded in a 50 °C oil bath for 4 hours. The crude product was washed with 1M HCl to remove excess amine, and the organic phase was collected and dried with MgSO₄. The organic phase was concentrated in vacuo to yield PDMS5k-NH₂. PDMS5k-NH₂ was converted to PDMS5k-NB by the same procedure stated above for PDMS2k-NB and purified by column chromatography using a DCM/hexanes gradient eluent, starting at 1:1 DCM:hexanes and gradually increasing the DCM content to 1:1 DCM:hexane. PDMS5k-NB: $M_n$ 5 240 g/mol (DP 75), $D$ 1.17, yield 582 mg (10 % isolated yield). $^1$H NMR spectra is provided in the Supplemental Information Figure S4.2. PDMS5k-NB H$^1$ NMR: δH (400 MHz, CDCl₃): -0.8-0.2 (m, 405H, -O-Si-2(CH₂)-), 0.48 (m, 4H, Si-CH₂-CH₂-), 0.79 (t, 3H, CH₂-CH₃), 1.18 (m, 2H, -CH₂-CH₂-CH₃), 1.25 (m, 2H, -CH₂-CH₂-CH₂-), 2.57 (s, 2H, CH-CH-CH₂-CH-), 3.2 (s, 2H, CH-CH-CH₂-CH-C-), 3.35 (t, 2H, -N-CH₂-CH₂-), 6.2 (s, 2H, -CH-CH=CH-CH-).

**Synthesis of PDMS bottlebrushes, P(NB-PDMS-X)n.** All reactions were carried out in an oxygen and water-free glove box. The following is a representative synthesis of P(PDMS2k)$_{100}$. PDMS2k-NB (100 mg, 0.043 mmol) was added to a glass vial, equipped with a stir bar. Anhydrous, degassed DCM was added to the vial for a final solution concentration of 0.05 M (0.8 mL). A stock solution of Grubb’s second generation catalyst solution was prepared in a separate vial (2.0 mg, 0.002 mmol, in 1.5 mL DCM). For a target backbone DP of 100, 0.0043 mmol of catalyst (100 μL) was added to the stirring macromonomer flask and allowed to react for 2 hours at room temperature. To quench the reaction, the vial was removed from the glove box and approximately 100 μL of butyl vinyl ether was added. The product is a viscous, semi-clear liquid and was concentrated in vacuo prior to characterization by GPC and NMR. The properties of PDMS bottlebrushes are presented in Table 4.1.
**Synthesis of linear PLA for matrix (PLA-18k).** Linear PLA was synthesized via ring opening polymerization of D, L-lactide in the presence of stannous octoate and a norbornenyl-alcohol using a procedure modified from a previous report. Lactide (15.3 mmol, 2.37 g), N-(hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide (0.22 mmol, 58.5 mg) and stannous octoate (0.13 mmol, 53 mg) were added to a 50 mL round bottom flask, and the flask was purged and backfilled with nitrogen three times. The reaction proceeded for 5 hours at 120 °C. The polymer was collected by precipitation in methanol and dried *in vacuo* to yield PLA-18k ($M_n$ 17500 g mol$^{-1}$ $D$ 1.36, yield 1.62 g, 68 % isolated yield).

**Synthesis of PLA macromonomer, PLA2k-NB.** PLA2k-NB was synthesized following the above procedure. Lactide (17.18 mmol, 2.47 g), N-(hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide (1.23 mmol, 0.31 g) and stannous octoate (0.04 mmol, 18 mg) reacted for 3 hours at 120 °C and collected by precipitation. PLA2k-NB ($M_n$ 2600 g/mol, $D$ 1.48, yield 1.70 g, 67 % isolated yield).

**Synthesis of PLA/PDMS Bottlebrush Copolymers, P(XPDMS-co-YPLA)$_{100}$**. All reactions were carried out in an oxygen and water-free glove box. In a representative procedure, PDMS2k-NB (50 mg, 0.018 mmol) and PLA2k-NB (46 mg, 0.018 mmol) were added to a clean glass vial, equipped with a stir bar. Anhydrous DCM was degassed by bubbling nitrogen. Stock catalyst solution was prepared in a second vial (1 mL, 1.8 μM Grubb’s modified second generation catalyst in DCM). DCM was added to the flask containing macromonomer to create a total molar concentration of PDMS and PLA macromonomer of 0.05 M (0.72 mL). Once dissolved, 100 μL of catalyst solution was added to the reaction vial and allowed to stir at room temperature for 2 hours before being quenched by the addition of butyl vinyl ether. Bottlebrush polymers were precipitated in cold methanol and dried *in vacuo* prior to characterization. See Table 4.2 properties of bottlebrush copolymers P(XPDMS-co-YPLA)$_{100}$.

**Synthesis of linear diblock additives, PDMS-b-PLA$_n$.** Linear block copolymers were prepared by ring-opening polymerization of $D,L$-lactide in the presence of amino-terminated PDMS (PDMS2k-NH$_2$) with stannous octoate as the catalyst. Three molecular weights were synthesized by varying the PLA block length (PDMS $M_n$ is held constant) as presented in Supplemental Information Table S4.1. The synthesis of...
PDMS(2700)-block-PLA(5700) is detailed here. PDMS2k-NH₂ was dried under vacuum pressure for 2 hours and D,L-lactide was recrystallized twice from ethyl acetate and dried in vacuum prior to use. PDMS2k-NH₂ (0.33 g, 0.124 mmol), D,L-lactide (0.688 g, 4.78 mmol) and stannous octoate (5.02 mg, 0.0124 mmol) were added to a microwave capsule equipped with a stirbar. The capsule was evacuated and backfilled with nitrogen three times before transferring into a glovebox under N₂ pressure where it was sealed. To the capsule 2M anhydrous toluene (2.4 mL, purged with N₂ for 20 minutes to remove oxygen) was added under nitrogen pressure. The reaction was heated to 130 °C for 30 minutes to ensure even mixing with microwaves followed by heating to 180 °C for 60 minutes. After reaction completion, toluene was removed by rotoevaporation and PDMS-block-PLA was collected by precipitation in cold methanol. Final product was analyzed by GPC and H¹ NMR. $M_n$ (GPC, by PS standards) 8830 g/mol, PDI 1.45. By NMR: $\text{DP}_{\text{PLA}}$ 51, $\text{DP}_{\text{PDMS}}$ 24. 32 % PDMS content.

**ROMP kinetics experiments.** The kinetics of macromonomer polymerization by ROMP were determined by GPC as a function of reaction time. Polymerization kinetics were analyzed for each macromonomer separately. Aliquots of the reaction were extracted at regular timed intervals (1, 2, 5, 10, 20, 30, 60, and 120 minutes), immediately quenched in butyl vinyl ether, and analyzed by gel-permeation chromatography (GPC). GPC spectra with refractive index detection for each aliquot contain a linear macromonomer peak (elution volume 17.3 – 19.5 mL) and a bottlebrush peak (elution volume 14 – 16 mL). A ratio of the integrated areas provides relative mass contents of macromonomer and bottlebrush, respectively.

**Film preparation.** All films, except those used for XPS, were cast on cleaned silica wafers. Wafers were cleaned by sonication in 2 wt% soap solution in water, DI water, and isopropyl alcohol for 30 minutes per solvent. After drying, polymer solutions (20 mg mL⁻¹ in chloroform) were spin casted for 60 s at 1500 rpm and 30 s at 300 rpm, typically producing films ~100 nm. Thermal annealing of films was performed by heating films to 100 °C for 2 hours on a hot plate in a nitrogen glove box and allowed to cool to room temperature before analysis.
4.3.2 Instrumentation

**Gel-Permeation Chromatography (GPC).** Polymer molecular weights and molecular weight dispersities were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10000 Å pore sizes), an Agilent variable wavelength UV/vis detector, a Wyatt technology HELEOS II multiangle laser light scattering (MALLS) detector (\(\lambda = 658\) nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/vis (SEC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer \(dn/dc\) values were calculated assuming 100% mass recovery and correcting the injected mass to account for unreacted macromonomer.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Proton-NMR (\(^1\)H NMR) spectra were recorded using tetramethylsilane as internal standard in CDCl\(_3\) on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm o.d. tubes with the concentration of 10 mg/mL.

**Differential Scanning Calorimetry (DSC).** DSC experiments were conducted employing two different protocols using a TA Instruments Q2000 calorimeter, calibrated for the liquid nitrogen cooling system (LNCS) using an indium standard and a helium flow rate of 25 mL/min. For samples involving PDMS, blends were placed in the calorimeter (using a Tzero aluminum pan) held at standby at 40 °C. The sample was cooled to -150 °C at a rate of 10 °C/min, held isothermally at -150 °C for 5 minutes, and subsequently heated to 0 °C at a rate of 10 °C/min and held at isothermally 0 °C for 5 minutes before starting another heating and cooling cycle. Bottlebrush copolymer samples were placed in the calorimeter (using a Tzero aluminum pan) held at standby at 40 °C. The sample was cooled to -150 °C at a rate of 10 °C/min, held isothermally at -150 °C for 5 minutes, and subsequently heated to 100 °C at a rate of 10 °C/min and held at isothermally 100 °C for 5 minutes before starting the cycle again. At least two cool/heat cycles were performed for each sample.
Contact Angle goniometry. Static contact angle measurements of DI water on polymer films were carried out using a Drop Shape Analyzer DSA 100 (Kruss Instruments) at ambient conditions. Water contact angles were measured immediately after contact with water. Measurements were repeated at least on three different spots per substrate per sample. The final reported values given represent an average and standard deviation of each film.

X-ray Photoelectron Spectroscopy (XPS, PHI Quantera SXM). XPS measurements were conducted using a PHI Quantera XPS, which uses a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a 50 W, 15 kV and 200 μm diameter X-ray beam for sample analysis. The XPS survey scan spectra were recorded in 0.5 eV steps with a pass energy of 140 eV. High resolution scan spectra of C1s were recorded in 0.1 eV steps with a pass energy of 26.0 eV. Low energy electrons and Ar+ ions were conducted for specimen neutralization in each measurement. The take-off angle is 45 degrees (penetration depth of 3 – 5 nm). Thin-film samples for XPS were prepared by dissolving polymer or polymer blends in chloroform at 20 mg/mL, filtering solutions and spin-casting onto cleaned ITO substrates at 1500 rpm for 60 s followed by 300 rpm for 30 s.

Atomic Force Microscopy (AFM). AFM analysis was performed using a Veeco Multimode 8 with NanoScope V Controller. Sample topography was recorded using ScanAsyst™ mode. 2nd order flattening was used for compensation of sample tilt and enhancement of image contrast.

Optical Microscopy (OM). Microscopy images were taken using a Zeiss Axioplan optical microscope in reflectance mode.

4.4 Results

4.4.1 PDMS Bottlebrush Polymer Synthesis and Characterization

PDMS bottlebrush polymers were synthesized using “grafting-through” ring-opening metathesis polymerization (ROMP) of norbornene-terminated PDMS macromonomers, as shown in Scheme 4.1. Norbornene-terminated PDMS macromonomers PDMS2k-NB and PDMS5k-NB were prepared by end-group modification of commercially available PDMS. For PDMS2k-NB, the amino terminus of PDMS2k-NH₂ was directly converted
to a ROMP-active norbornene group by condensation with NB-OH in the presence of triethyl amine (see Scheme 4.1) and confirmed by a shift in the $^1$H NMR signal corresponding to the methyl proton adjacent to the amine from 2.65 to 3.33 ppm. For PDMS5k-NB an additional step was necessary to convert a silane terminus to an amine, which was followed by condensation with NB-OH yielding PDMS5k-NB. $^1$H NMR confirmed the reaction of silane end groups after the first step by the disappearance of a peak at $\delta = 4.65$ ppm. The methyl protons adjacent to the silane group (HSi-$CH_2$-) shift from 4.65 to 2.65 ppm. After the condensation reactions, NMR showed peaks corresponding to the norbornene endgroup at 6.26 ppm and 2.64 ppm. $^1$H NMR spectra for the purified products are presented in the Supplemental Information Figures S4.1 and S4.2.

Scheme 4.1 Synthesis of PDMS bottlebrush polymers P(PDMS-$X$)$_n$, where $X$ denotes the molecular weight of each side-chain in g/mol and $n$ denotes the target degree of polymerization (DP) of backbone.
Table 4.1 Chemical and thermal properties of PDMS bottlebrush polymers P(PDMS-X)_n, where X denotes the molecular weight of each side-chain in g/mol and n denotes the degree of polymerization (DP) of backbone.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ $^a$ [g/mol]</th>
<th>$D$ $^b$</th>
<th>$M_w$ $^c$ [g/mol]</th>
<th>[MM]/[cat.]</th>
<th>DP$_{BB}$ $^d$</th>
<th>Conv.$^e$</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PDMS2k)$_{31}$</td>
<td>47 900</td>
<td>1.15</td>
<td>87 000</td>
<td>50</td>
<td>31</td>
<td>82</td>
<td>-123</td>
</tr>
<tr>
<td>P(PDMS2k)$_{58}$</td>
<td>53 000</td>
<td>1.16</td>
<td>115 000</td>
<td>100</td>
<td>58</td>
<td>86</td>
<td>-123</td>
</tr>
<tr>
<td>P(PDMS2k)$_{69}$</td>
<td>67 000</td>
<td>1.48</td>
<td>193 000</td>
<td>200</td>
<td>69</td>
<td>86</td>
<td>-124</td>
</tr>
<tr>
<td>P(PDMS2k)$_{99}$</td>
<td>82 000</td>
<td>1.91</td>
<td>276 000</td>
<td>300</td>
<td>99</td>
<td>87</td>
<td>-123</td>
</tr>
<tr>
<td>P(PDMS5k)$_{39}$</td>
<td>62 000</td>
<td>1.16</td>
<td>146 700</td>
<td>50</td>
<td>39</td>
<td>87</td>
<td>-122</td>
</tr>
<tr>
<td>P(PDMS5k)$_{59}$</td>
<td>93 000</td>
<td>1.21</td>
<td>296 500</td>
<td>100</td>
<td>59</td>
<td>83</td>
<td>-122</td>
</tr>
<tr>
<td>P(PDMS5k)$_{130}$</td>
<td>117 000</td>
<td>1.40</td>
<td>654 300</td>
<td>150</td>
<td>130</td>
<td>82</td>
<td>-122</td>
</tr>
<tr>
<td>P(PDMS5k)$_{139}$</td>
<td>112 700</td>
<td>1.49</td>
<td>699 000</td>
<td>300</td>
<td>139</td>
<td>88</td>
<td>-123</td>
</tr>
</tbody>
</table>

$^a$ $M_n$ by GPC relative to monodisperse PS standards. $^b$ From GPC relative to monodisperse PS standards. $^c$ $M_w$ calculated from GPC light-scattering analysis. $^d$ Calculated using number-averaged molecular weights $M_n$ for sidechains and $M_w$ bottlebrush polymer. $^e$ Calculated using relative mass values from GPC.
Figure 4.4 Gel permeation chromatography (GPC) traces of PDMSX-NB macromonomers (dashed lines) and P(PDMS-X)n bottlebrush polymers (solid lines) with 2 kg/mol (top) and 5 kg/mol (bottom) PDMS side-chains.

ROMP of the PDMS macromonomers produced PDMS bottlebrushes with 2 and 5 kg/mol side-chains and backbone DPs up to 139. Detailed properties of all PDMS bottlebrush polymers are presented in Table 4.1. PDMS bottlebrush polymers with 2 kg/mol side-chains were synthesized with backbone DPs up to 99, resulting in molecular weights as high as 276 000 g/mol. PDMS bottlebrush polymers with 5 kg/mol side-chains were synthesized with backbone DPs up to 139 with molecular weights reaching 699 000 g/mol. The molecular weight dispersity $D$ was below 1.5 for all samples except for P(PDMS2k)99, which had a $D$ of 1.9. The mass conversion of macromonomers was quantified by GPC and was between 82 and 88 wt % for all samples (Figure 4.4). $^1$H NMR of the final product showed no evidence of norbornene protons ($\delta = 6.5$ ppm), and
therefore the unreacted materials can be attributed to unfunctionalized PDMS polymer. Based on the mass conversion during ROMP, the macromonomer purity is estimated to be 88% and 87% for PDMS2k-NB and PDMS5k-NB, respectively.

Thermal properties of PDMS bottlebrushes were studied by differential scanning calorimetry (DSC). All bottlebrush PDMS bottlebrush polymers exhibited a glass transition temperature, \( T_g \), a crystal melting temperature, \( T_m \), and a crystallization temperature, \( T_c \) (see Supplemental Information Figures S4.3 and S4.4). These transition temperatures were found to be independent of bottlebrush DP and only weakly dependent on side-chain molecular weight, as shown in Table 4.2.

**Table 4.2** Summary of thermal properties of PDMS bottlebrush polymers with 2k and 5k side-chains.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g )</th>
<th>( T_c )</th>
<th>( T_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PDMS2k)(_{31})</td>
<td>-123.3</td>
<td>-75.24</td>
<td>-54.92</td>
</tr>
<tr>
<td>P(PDMS2k)(_{58})</td>
<td>-122.8</td>
<td>-79.72</td>
<td>-52.89</td>
</tr>
<tr>
<td>P(PDMS2k)(_{69})</td>
<td>-123.8</td>
<td>-74.85</td>
<td>-53.71</td>
</tr>
<tr>
<td>P(PDMS2k)(_{99})</td>
<td>-123.4</td>
<td>-74.94</td>
<td>-55.34</td>
</tr>
<tr>
<td>P(PDMS5k)(_{39})</td>
<td>-122.3</td>
<td>-82.57</td>
<td>-47.98</td>
</tr>
<tr>
<td>P(PDMS5k)(_{59})</td>
<td>-122.4</td>
<td>-88.83</td>
<td>-49.58</td>
</tr>
<tr>
<td>P(PDMS5k)(_{130})</td>
<td>-122.2</td>
<td>-85.79</td>
<td>-47.96</td>
</tr>
<tr>
<td>P(PDMS5k)(_{139})</td>
<td>-122.6</td>
<td>-79.09</td>
<td>-47.67</td>
</tr>
</tbody>
</table>

4.4.2 Synthesis of PDMS/PLA bottlebrush copolymers

Bottlebrush copolymers with mixed PDMS and PLA side-chains were synthesized in a one-pot grafting-through ROMP of both PLA and PDMS macromonomers (Scheme 4.2).
The resulting bottlebrush copolymers have PDMS and PLA side-chains and are denoted as $P(\chi_{\text{PDMS-co-PLA}})_{100}$, where $\chi$ and $\gamma$ represent the molar fraction of PDMS and PLA side-chains, respectively. To investigate the polymer properties as a function of side-chain composition, we systematically decreased the amount of PDMS side-chains in each bottlebrush copolymer while keeping the target backbone DP constant ($n = 100$). The resulting copolymers, $P(75\text{PDMS-co-25PLA})_{100}$, $P(50\text{PDMS-co-50PLA})_{100}$, and $P(25\text{PDMS-co-75PLA})_{100}$, had final compositions of 73, 45, and 22 mol% PDMS2k-NB, respectively (see Table 4.3). The PDMS composition of the bottlebrush copolymers was slightly lower than the target composition, due to the presence of unfunctionalized PDMS macromonomer. All bottlebrush copolymers were solid at room temperature, even with only 25 mol% PLA side-chains, allowing for purification by precipitation in methanol to remove unreacted PDMS macromonomer. Bottlebrush copolymer polymer purity was confirmed by GPC to be greater than 98% in all cases.

Scheme 4.2 Synthesis of bottlebrush copolymers $P(\chi_{\text{PDMS-co-PLA}})_{n}$ with mixed PDMS and PLA sidechains is carried out in a one-pot ROMP. The resulting polymers have 75, 50, or 25 mol % PDMS sidechains.
Table 4.3 Properties bottlebrush copolymers with PDMS and PLA size-chains

<table>
<thead>
<tr>
<th>Sample</th>
<th>mol % PDMS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;[g/mol]&lt;sup&gt;c&lt;/sup&gt;</th>
<th>dn/dc</th>
<th>% BB&lt;sup&gt;d&lt;/sup&gt;</th>
<th>T&lt;sub&gt;Tg,PDMS&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;Tg,PLA&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(75PDMS-co-25PLA)&lt;sub&gt;100&lt;/sub&gt;</td>
<td>73.0</td>
<td>1.24</td>
<td>132 000</td>
<td>0.025</td>
<td>99</td>
<td>-122.2</td>
<td>37.9</td>
</tr>
<tr>
<td>P(50PDMS-co-50PLA)&lt;sub&gt;100&lt;/sub&gt;</td>
<td>44.8</td>
<td>1.32</td>
<td>162 000</td>
<td>0.040</td>
<td>98</td>
<td>-121.8</td>
<td>45.7</td>
</tr>
<tr>
<td>P(25PDMS-co-75PLA)&lt;sub&gt;100&lt;/sub&gt;</td>
<td>22.2</td>
<td>1.28</td>
<td>153 500</td>
<td>0.048</td>
<td>100</td>
<td>----</td>
<td>47.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Percentage of PDMS side-chains in final bottlebrush copolymer, as determined by NMR.  
<sup>b</sup> From GPC relative to monodisperse PS standards.  
<sup>c</sup> M<sub>w</sub> calculated from GPC light-scattering analysis.  
<sup>d</sup> Mass fraction of bottlebrush polymer in the final isolated product, determined by GPC relative to PS standards. The remaining fraction is free PDMS homopolymer.

The distribution of side-chains along the backbone was determined by the ROMP kinetics of each macromonomer and the initial concentrations of PLA and PDMS macromonomers. We determined the reaction rates of PLA2k-NB and PDMS2k-NB separately (shown in Figure 4.5). Generally we would like to know if the side-chains are distributed randomly (equal kinetics) or in a gradient (one macromonomer reacts faster) along the backbone, as this could affect the miscibility of copolymers in thin films. We found that PLA2k-NB reacts approximately 2.5 times faster than PDMS2k-NB. Therefore, with equal or higher initial concentrations of PLA macromonomers (such as in the case of P(50PDMS-co-50PLA)<sub>100</sub> and (P(25PDMS-co-75PLA)<sub>100</sub>, we expected a gradient distribution of side-chains along the backbone consisting of a “PLA-rich” segment on one end and “PDMS-rich” segment on the opposite end. The distribution of side-chains in P(75PDMS-co-25PLA)<sub>100</sub> is expected to be nearly statistical. The absolute ratios of PDMS to PLA sidechains in the bottlebrush copolymers were determined by <sup>1</sup>H NMR analysis of the final products after precipitation. Thermal properties of bottlebrush copolymers were analyzed by differential scanning calorimetry. P(75PDMS-co-25PLA)<sub>100</sub> and P(50PDMS-co-50PLA)<sub>100</sub> exhibit two thermal glass transitions, corresponding to PDMS (near -122 °C) and PLA (near 45 °C) (see Table 4.3 and Supplemental Information Figure S4.5). The bottlebrush copolymer with the lowest
PDMS content, P(25PDMS-co-75PLA)\textsubscript{100}, only exhibits a single $T_g$ near 47 °C corresponding to the PLA side-chains. The PLA $T_g$ is 8 °C lower in P(75PDMS-co-25PLA)\textsubscript{100} compared with the other bottlebrush copolymers, indicating that the PLA chains are plasticized by the flexible, low $T_g$ PDMS polymers, as has been observed for PLA blends.\textsuperscript{37} No PDMS crystallization is observed in any bottlebrush copolymer sample.

**Figure 4.5** (top) GPC traces for PDMS/PLA bottlebrush copolymers and starting macromonomers showing minimal traces of macromonomer in final copolymer product. (bottom) ROMP kinetics for PDMS2k-NB (black squares) and PLA2k-NB (red circles) macromonomers showing faster polymerization rate for PLA2k-NB. Kinetics measurements are carried out for each macromonomer separately. Initial conditions: $[\text{MM}]_0 = 0.05$ M in DCM and $[\text{MM}]/[\text{catalyst}] = 100$. 
We characterized the surface properties of pure bottlebrush copolymer films with thickness of approximately 100 nm. The water contact angles (WCA) of P(75PDMS-co-25PLA)$_{100}$, P(50PDMS-co-50PLA)$_{100}$ and P(25PDMS-co-75PLA)$_{100}$ bulk films were 107 ± 1°, 108 ± 0.3°, and 95 ± 0.7°, respectively. Interestingly, the WCA of P(75PDMS-co-25PLA)$_{100}$ films is the same as pure PDMS elastomer (Table 4.3), suggesting that side-chains can partially phase-separate along the main backbone to form a pure PDMS wetting layer at the free surface. While all films were hydrophobic, the extent of hydrophobicity increased with PDMS composition. Optical microscopy of P(75PDMS-co-25PLA)$_{100}$ films were uneven and rough, whereas P(50PDMS-co-50PLA)$_{100}$ and P(25PDMS-co-75PLA)$_{100}$ films appear to be smooth (Supplemental Information Figure S4.6). The roughness in bottlebrushes with high PDMS content is expected, as these materials are more liquid-like.

### 4.4.3 Bottlebrush copolymer additives and thin-film properties

In prior work with nearly athermal blends of bottlebrush and linear polymers,$^{11}$ we demonstrated that miscibility is controlled by relative lengths of matrix and bottlebrush side-chains ($N_m/N_{sc}$). When $N_m/N_{sc} < 2$, the matrix polymer could "wet" the bottlebrushes and enabled their dispersion. When $N_m/N_{sc} > 8$, the bottlebrushes were no longer wettable, so the constituents underwent a slow demixing process that drove the bottlebrushes to the interfaces; this allowed linear chains to gain conformational entropy in the interior of the film. In the present study, we consider the behavior in non-athermal systems of bottlebrush PDMS/PLA copolymers in blends with linear PLA (18 kg/mol), where $N_m/N_{sc} \sim 7$, $f_{PDMS} = 25, 50, \text{or } 75 \text{ mol }\% \text{ PDMS}$, and the bottlebrush loading is either 1 or 5 wt %. PDMS and PLA are highly incompatible (Flory-Huggins segment-segment interaction parameter $\chi \approx 1.4$ at 298 K for a reference volume of 118 Å$^3$)$^{38-39}$ so PLA bottlebrush arms will act as compatibilizers to stabilize the bottlebrush additives in the film. The surface energies of PDMS and PLA are 19.8 mN/m and 42 mN/n, respectively,$^{40-42}$ therefore we expect PDMS-based bottlebrushes to de-mix and accumulate at the air interface. We anticipate that bottlebrushes may also accumulate at
the bottom interface,\textsuperscript{43-44} but the objective of these studies is to tailor surface properties, so we do not emphasize characterization of the buried interface in this work.

To determine if bottlebrush copolymers spontaneously segregate to the top of thin film blends, we first measured the water contact angle (WCA) for bulk PLA films and found a value of 65.7 ± 1°. As a reference, bulk PDMS is extremely hydrophobic with a water contact angle of 107 ± 1.3°. We then measured the WCA for all blends and observed significant increases (by more than 20°) with only 1 wt % bottlebrush. Blends with 5 wt % bottlebrush additives showed further increases in contact angle, up to 30°. Therefore, bottlebrush copolymer additives accumulate at the free surface and introduce hydrophobic behavior, where the extent of hydrophobicity is enhanced with loading. Contact angles as a function of bottlebrush copolymer loading and side-chain composition are reported in Table 4.3 and Figure 4.6. All films are hydrophobic (WCA > 90°), with the exception of 1 wt % P(25PDMS-co-75PLA)\textsubscript{100} which has a WCA of 85° owing to the high PLA content and the low loading of the material. The WCA for 5 wt % blends increased by an average of 6.1° compared with the 1 wt % blends for all compositions of additives. Similar to results from pure bottlebrush copolymer contact angles, a higher content of PDMS side-chains in the copolymer additives results in higher contact angle values for the blends. In all cases, the water contact angle for blends was less that the value for the corresponding pure bottlebrush copolymer, indicating the presence of some PLA at the top film interface.
Figure 4.6 Change in water contact angle (WCA) of films blended with 1 wt % (gray bar) or 5 wt % (black bar) bottlebrush copolymers in bulk PLA with respect to WCA of bulk PLA films. Copolymer additives, $\text{P}(\text{XPDMSe-co-YPLA})_{100}$, are labeled by the ratio of PDMS (X) to PLA (Y) side-chains such that 75/25, 50/50 and 25/75 represent blends of $\text{P}(75\text{PDMS-co-25PLA})_{100}$, $\text{P}(50\text{PDMS-co-50PLA})_{100}$, and $\text{P}(25\text{PDMS-co-75PLA})_{100}$ respectively. PLA films without bottlebrush additive have a water contact angle of 65.7 ± 1°. Lines mark the contact angle for pure bottlebrush copolymers of the same side-chain composition referenced to PLA.

Film uniformity and stability were evaluated by optical microscopy of blend films immediately after spin-casting and after thermal annealing. Bulk PLA films are smooth and featureless before and after annealing, while obvious phase separation is observed in PLA films containing either 1 or 5 wt % linear PDMS additive (Figure 4.7, and Supplemental Information Figures S4.7 and S4.8). Blend films with bottlebrush copolymer additives are uniform both before and after thermal annealing, with the exception of films with a 5% loading of $\text{P}(75\text{PDMS-co-25PLA})_{100}$. This suggests that PLA side-chains are effective compatibilizers to prevent large-scale phase separation, but at sufficiently high PDMS content and loading bottlebrush copolymers phase separate. The nanoscale morphology of the film surface was further analyzed by both AFM and dark-field microscopy measurements and is discussed below.
**Figure 4.7** Optical micrographs of films cast with 5 wt% bottlebrush copolymer additives (A – F) and linear PDMS (G-H) before and after thermal annealing (right column). A, B) \( P(25\text{PDMS-co-75PLA})_{100} \); C, D) \( P(50\text{PDMS-co-50PLA})_{100} \); E, F) \( P(75\text{PDMS-co-25PLA})_{100} \); G, H) linear PDMS2k. Scale bar 50 μm.

The contact angle and microscopy results indicate that bottlebrush copolymer additives segregate to the top film surface without large-scale phase segregation, with the exception of 5 wt % \( P(75\text{PDMS-co-25PLA})_{100} \). For comparison, a series of PDMS-\( b \)-PLA diblock copolymers with roughly 25, 50, and 75 wt % PDMS were synthesized and used as additives in PLA films (see Supplemental Information Table S4.1). Blend films
with 1 and 5 wt % diblock copolymer additives appeared uniform before and after thermal annealing (See Supplemental Information Figures S4.7 and S4.8). As expected, PDMS- b-PLA additives increase the film WCA due to segregation to the film surface, but the increase in WCA is smaller compared with bottlebrush copolymer additives. Linear diblock additives increased the WCA up to 87.3° and 96.5° for 1 and 5 wt % loading compared with 93.4° and 99.5° for bottlebrush copolymer additives (Table 4.4 and Supplemental Information Table S4.1). The difference is greater than the uncertainty in the WCA values, which is less than 1° for all samples. The stronger effect of bottlebrushes may be due to a combination of enthalpic and entropic effects that drive bottlebrushes to interfaces, and demonstrates that different surface functionalities could be introduced to the film surface by carefully designed bottlebrush polymer additives. While here we focus only on bottlebrush copolymers with PDMS side-chains, a variety of polymer side-chains can be incorporated using the same materials synthesis approach. Diblock copolymers may also be forming micelles rather than segregating to the film interface. The contact angle values of blend films containing linear diblock copolymer decreased with higher PDMS compositions in the diblock, which is consistent with the formation of diblock copolymer micelles in the film interior.

### Table 4.4 Contact angle results for blends cast with linear diblock additives.

<table>
<thead>
<tr>
<th>Polymer structure</th>
<th>name</th>
<th>% PDMS</th>
<th>1% cast (°)</th>
<th>5% cast (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS(2k)-AM</td>
<td>PDMS2k</td>
<td>100%</td>
<td>90.1 ± 0.6</td>
<td>90.2 ± 0.5</td>
</tr>
<tr>
<td>PDMS(2700)-b-PLA(550)</td>
<td>BCP83</td>
<td>83</td>
<td>84.4 ± 0.7</td>
<td>88.9 ± 0.6</td>
</tr>
<tr>
<td>PDMS(2700)-b-PLA(2700)</td>
<td>BCP50</td>
<td>50</td>
<td>86.1 ± 0.4</td>
<td>95.2 ± 1.0</td>
</tr>
<tr>
<td>PDMS(2700)-b-PLA(5700)</td>
<td>BCP32</td>
<td>32</td>
<td>87.3 ± 0.3</td>
<td>96.5 ± 0.3</td>
</tr>
</tbody>
</table>

Blend films containing bottlebrush copolymers were analyzed by XPS to determine the composition at the top surface. The data from XPS analysis corresponds to the elemental composition within the top 3 – 5 nm of each film, and PDMS homopolymer, PLA homopolymer, and pure bottlebrush copolymers were measured as references. XPS data were analyzed by comparing relative peak areas between carbon, oxygen and silicon (Cm.
O
m, and Si
m) and adjusting for sensitivity factors (Table 4.5. We also calculated the expected peak ratios for carbon, oxygen and silicon (C
, O
 and Si
) based on the known chemical structures for PDMS and PLA polymers and assuming uniform mixing of PDMS and PLA in the films (see SI for a detailed explanation). For the single component films, the measured and calculated C:O ratios were generally in good agreement, within 4 % for most samples. Qualitatively, the measured Si contents trend as expected: P(75PDMS-co-25PLA)
 has the highest Si content, and P(25PDMS-co-75PLA)
 has the lowest. We measured higher Si contents in (50PDMS-co-50PLA)
 and P(25PDMS-co-75PLA)
 relative to the calculated values, while the Si content was lower than the calculated value for P(75PDMS-co-25PLA)
. This suggests that the PDMS side-chains may segregate toward the top film surface when the PDMS content is low, while the side-chains are more uniformly mixed for P(75PDMS-co-25PLA)
.
Table 4.5 Compositional values of C, O, and Si for calculated values and measured results, determined by XPS measurements in pure component and blend thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated Ratios</th>
<th>Measured Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;c&lt;/sub&gt;</td>
<td>O&lt;sub&gt;c&lt;/sub&gt;</td>
</tr>
<tr>
<td>Linear PLA</td>
<td>60.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Linear PDMS</td>
<td>50.0</td>
<td>25.0</td>
</tr>
<tr>
<td>P(75PDMS-co-25PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>52.7</td>
<td>29.1</td>
</tr>
<tr>
<td>P(50PDMS-co-50PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>55.5</td>
<td>33.3</td>
</tr>
<tr>
<td>P(25PDMS-co-75PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>57.8</td>
<td>36.7</td>
</tr>
<tr>
<td>1% P(75PDMS-co-25PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>59.9</td>
<td>39.9</td>
</tr>
<tr>
<td>5% P(75PDMS-co-25PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>59.7</td>
<td>39.5</td>
</tr>
<tr>
<td>1% P(50PDMS-co-50PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>60.0</td>
<td>39.9</td>
</tr>
<tr>
<td>5% P(50PDMS-co-50PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>59.8</td>
<td>39.7</td>
</tr>
<tr>
<td>1% P(25PDMS-co-75PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>60.0</td>
<td>40.0</td>
</tr>
<tr>
<td>5% P(25PDMS-co-75PLA) &lt;sub&gt;100&lt;/sub&gt;</td>
<td>59.9</td>
<td>39.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> XPS data from PDMS films reported by Sabata et. al. <sup>45</sup>

<sup>b</sup> Estimated from measurements of PDMS elastomer prepared from Sylgard 184.

In the case of bottlebrush blends, the predicted elemental ratios were calculated from a mass balance by assuming the bottlebrushes were uniformly distributed throughout the thickness of the film (i.e. the calculated surface composition is the same as the bulk composition). If bottlebrush copolymers segregated to the free surface, then we should observe a higher measured Si content relative to calculated values. As shown in Table 4.5 and Figure 4.8, XPS results for blends reveal a large increase in the Si content over the expected values. This demonstrates an excess of bottlebrush at the surface of the films.
which is consistent with water contact angle measurements. The 1 wt % blends show 2 – 5 mol % Si content, whereas the expected content is less than 0.2 mol % for a homogeneous distribution of bottlebrush. The 5 wt % blends show a larger increase in the Si content, with Si compositions of 9.7, 5.8, and 3.1 mol % for P(75PDMS-co-25PLA)$_{100}$, P(50PDMS-co-50PLA)$_{100}$, and P(25PDMS-co-75PLA)$_{100}$, respectively. Blends with 5 wt % bottlebrush copolymer have a higher Si content than the 1 wt % blends, as expected.

![Figure 4.8 XPS survey data for bottlebrush copolymer sample P(75PDMS-co-25PLA)$_{100}$ for films cast from 1 wt% blend (blue), 5 wt% blend (red) and 100 % bulk copolymer (black). Inset shows silicon signal increases with bottlebrush copolymer loading. Elemental compositions are calculated from oxygen (O $1s$), carbon (C $1s$) and silicon (Si $2p$) signals present in all cases.](image)

The measured silicon content is used to determine the mass fraction of each blend at the top surface. Based on measured XPS C$_m$:O$_m$:Si$_m$ ratios for blends and homopolymer bottlebrush films, we determined the mass fraction of bottlebrush at the surface is between 17 and 21 wt % for 1 wt % blends, and between 32 and 36 wt % for the 5 wt % blends. These results combined with contact angle and optical microscopy measurements prove that bottlebrush copolymers spontaneously segregate to the polymer-air interface during spin casting without macroscopic phase separation. Interestingly, the bottlebrush content of the top surface appears to be roughly independent of the PDMS content in the
bottlebrush copolymers, and the highest bottlebrush content at the top surface was measured for blends with P(25PDMS-co-75PLA)\textsubscript{100}.

To further investigate the morphology of bottlebrush copolymer blend films, we characterized all films by AFM and dark field optical microscopy. The surfaces of all films exhibit round depressions in AFM height images (see Figure 4.9 for 1 wt % films and Supplemental Information Figures S4.9 and S4.10). One might imagine these features are PDMS domains, and the AFM tip is "sinking" when contacting these rubbery regions.\textsuperscript{39} However, we assign these features as holes based on the following arguments: First, AFM analysis reveals similar features in pure PLA films, as shown in Figure 4.9 G and Supplemental Information S4.11. Other studies have found similar holes in PLA fibers and films attributed to evaporative cooling and condensation of water droplets on the surface.\textsuperscript{46-47} Second, the depressions are at least 10 nm deep. (The actual depth could be larger, but the tip geometry cannot reach the bottom of high aspect ratio nanostructures.) If the depressions are PDMS-rich domains, then most of the bottlebrushes would be located in these domains rather than on the surface of the film. However, WCA measurements and XPS data suggest that the surfaces are covered with a nearly conformal layer of bottlebrush copolymer. Third, dark field optical microscopy clearly demonstrates that these features are associated with significant topography: The edges of these features are strongly scattering, which is expected for deep holes. These data are reported in Supplemental Information Figure S4.12. Finally, AFM phase images (Supplemental Information Figure 4.13) are also consistent with holes: The tip "skips" at the leading edge of the features, a common artifact with high-aspect-ratio topography.
Figure 4.9: AFM images of bottlebrush copolymer blend films with 1 wt % bottlebrush. A,B) P(25PDMS-co-75PLA)\textsubscript{100}; C,D) P(50PDMS-co-50PLA)\textsubscript{100}; E,F) P(75PDMS-co-25PLA)\textsubscript{100}. Linecuts at the bottom are for as-cast (left) and annealed (right) P(75PDMS-co-25PLA)\textsubscript{100}. G) AFM height image of pure, un-annealed PLA film along with a line-cut of the depth profile.
4.5 Conclusions

We demonstrate the synthesis of PDMS bottlebrush polymers and PDMS/PLA bottlebrush copolymers by ROMP. This synthesis method enables the preparation of well-defined, highly branched PDMS bottlebrush polymers and copolymers. These materials exhibit surfactant-like properties in thin film blends with linear PLA: Both contact angle goniometry and XPS demonstrate a spontaneous accumulation of these additives at the film surface without lateral phase segregation. Linear PDMS is found to phase separate strongly while PDMS-\textit{b}-PLA do not enrich the film surface as strongly as bottlebrush copolymer additives. This work demonstrates that low-surface energy bottlebrush copolymer additives can be used to introduce new surface properties in polymer films, such as creating a hydrophobic surface in a hydrophilic polymer film, which has potential applications in fouling reduction. Future work will explore the use of tailored bottlebrush copolymers to introduce different surface functionalities through entropically- and enthalpically-mediated segregation.

4.6 References


11. Mitra, I. L.; Xianyu; Pesek, Stacy L.; Makarenko, Boris; Lokitz, Brad S.; Uhrig, David; Ankner, John F.; Verduzco, Rafael; Stein, Gila E., Thin Film Phase Behavior of Bottlebrush/Linear Polymer Blends. *Macromolecules* **2014**.


4.7 Supporting Information

Figure S4.1 $^1$H NMR spectroscopy for PDMS2k-NH$_2$ as received and PDMS2k-NB after attaching a terminal norbornene group by amino condensation.
Figure S4.2 $^1$H NMR spectroscopy for (top) PDMS5k-SiH as received, showing silane protons at $\delta$ 4.7, (middle) PDMS5k-NH$_2$ with the presence of amino protons at $\delta$ 2.7, and (bottom) PDMS5k-NB after attaching a terminal norbornene group by amino condensation.
Figure S4.3 DSC thermographs of PDMS bottlebrush polymers with 2 kg/mol side-chains, P(PDMS2k)ₙ. The $T_g$ of these polymers did not change with overall molecular weight or backbone DP.
Figure S4.4 DSC thermographs of PDMS bottlebrush polymers with 5 kg/mol side-chains, $P(PDMS5k)_n$. The $T_g$ of these polymers did not change with overall molecular weight or backbone DP.
Figure S4.5 DSC thermographs of bottlebrush copolymers P(XPDMS-co-YPLA)\textsubscript{100} with mixed PDMS\textsubscript{2k} (molar fraction denoted by $X$) and PLA\textsubscript{2k} (molar fraction denoted by $Y$). The $T_g$ of PDMS (around -122°C) was suppressed by increasing PLA content ($T_g$ PLA around 50 °C).

Figure S4.6 Polarized Optical microscopy images of bottlebrush copolymer films. Increased PLA content shows smoother, more stable films after casting from solutions of 20 mg/mL in chloroform onto silica wafers. Scale bars 50 μm.
Table S4.1 Properties of PDMS-b-PLA linear diblock polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Lactide</th>
<th>DP PLA</th>
<th>$M_n,_{GPC}$</th>
<th>$M_n,_{NMR}$</th>
<th>PDI</th>
<th>% PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS(2700)-b-PLA(550)</td>
<td>1:8.9</td>
<td>5</td>
<td>5600</td>
<td>2137</td>
<td>1.29</td>
<td>83</td>
</tr>
<tr>
<td>PDMS(2700)-b-PLA(2700)</td>
<td>1:20.9</td>
<td>26</td>
<td>6700</td>
<td>3800</td>
<td>1.19</td>
<td>50</td>
</tr>
<tr>
<td>PDMS(2700)-b-PLA(5700)</td>
<td>1:37.1</td>
<td>51</td>
<td>8800</td>
<td>5485</td>
<td>1.45</td>
<td>32</td>
</tr>
</tbody>
</table>

Figure S4.7 Optical micrographs of blends from 1% linear PDMS and 1% linear diblock “as cast” (top row) and after thermal annealing (100 °C, 2 hrs). Linear PDMS as an additive results in phase separation with heating. Scale bar 50μm.
Figure S4.8 Optical micrographs of blends from 5% linear PDMS and 5% linear diblock “as cast” (top row) and after thermal annealing (100 °C, 2 hrs). Linear PDMS as an additive results in phase separation with heating. Scale bar 50μm.

Figure S4.9 AFM height images for 1 wt % bottlebrush copolymer films blended with linear PLA before and after thermal annealing for 2 hours at 100 °C. Linecuts along the bottom are for annealed films.
Figure S4.10 AFM height images for 5 wt % bottlebrush copolymer films blended with linear PLA before and after thermal annealing for 2 hours at 100 °C. Line-cuts along the bottom are for annealed films.

Figure S4.11 AFM height images for pure PLA and P(75PDMS-co-25PLA)100 showing similar "holes" as observed in bottlebrush copolymer blends.
Figure S4.12 Bright and dark-field microscopy analysis of bottlebrush blend films, before and after thermal annealing. Dark-field microscopy reveals topographical features in the films, consistent with the interpretation of holes present in the films.
Figure S4.13 Tapping mode height (left) and phase (right) images for 1% P(75PDMS-co-25PLA)_{100}.

SUPPLEMENT-
Explanation of XPS calculations:

Calculated elemental ratios

1. For homopolymers

Only the repeat unit of each polymer chain is considered. The norbornene unit contributes an undetectable amount of N to the XPS patterns and the mass % of NB is significantly less than the polymer chains. The elemental ratios are determined from the structures of the repeat units:

\[
\text{PLA: } \text{C:O:Si} :: 3:2:0 = 60:40:0 \quad \text{PDMS: } \text{C:O:Si} :: 2:1:1 = 50:25:25
\]

2. For PDMS/PLA bottlebrush copolymer film and blend films:

Expected elemental compositions are calculated assuming a uniform blend of PDMS and PLA bottlebrush side-chains and PLA matrix polymer, where applicable. Polymer endgroups and the polynorbornene backbone are neglected in our calculation of elemental composition.
The total mass fraction of PLA and PDMS is calculated using the known mass fractions of the PLA and PDMS side-chains in the bottlebrushes and, where applicable, the mass fraction of bottlebrush polymer and linear PLA chains in the blend films. Next, the molar fraction of PLA repeat units is calculated using the molecular weight for each PLA (57 g/mol) and PDMS (74 g/mol) repeat unit. The elemental ratios shown above for PLA and PDMS repeat units are then weighted by the appropriate molar fractions of repeat units to calculate the expected elemental composition for the uniform bottlebrush film and bottlebrush blend films.

In the expressions below, PDMS % represents the molar fraction of PDMS repeat units and PLA % represents the molar fraction of PLA repeat units:

\[
\begin{align*}
C &= (\text{PDMS } \%) (0.5) + (\text{PLA } \%) (0.6) \\
O &= (\text{PDMS } \%) (0.25) + (\text{PLA } \%) (0.4) \\
\text{Si} &= (\text{PDMS } \%) (0.5) + (\text{PLA } \%) (0)
\end{align*}
\]

3. Calculation of concentration of bottlebrush copolymer in top surface (3-5 nm)

All the Si content measured at the film surface is due to bottlebrush copolymer since PLA has no Si. For a measured Si elemental composition, the expression above provides a molar fraction of PDMS repeat units. This can be used to calculate the mass fraction of PDMS repeat units and, since the mass fraction of PDMS in the bottlebrushes is known, this can be used to calculate mass fraction of BBP in the top surface.

4.8 Appendix I: Self-assembly of bulk PDMS-PLA bottlebrush copolymers

The self-assembly of blocky and mixed bottlebrush copolymers with PDMS and PLA side-chains was investigated in thin films by grazing incidence small-angle x-Ray scattering (GI-SAXS). If ordered features exist on the surface of thin-films, SAXS data will have rings or bands in either $q_y$ or $q_z$ (Figure 4.22). Line-cuts along the $q_y$ or $q_z$ direction identify peak positions in $q$-space which can be converted to nanometer feature spacing by the relation $d = (2\pi)/q \ [\text{Å}^{-1}]$. For lamellar features, peaks $q1:q2:q3$ will scale as $1:2:3$. 

111
Figure S4.14 SAXS data for as-cast P(50PDMS-co-50PLA)_{100} showing ordered features along \( q_z \) consistent with lamellar stacking (in or out) of plane. (\( \theta = 0.15 \)).

Mixed-arm bottlebrush copolymers P(XPDMS-co-YPLA)_{100} (synthesis and sample details presented in Section 4.4, Scheme 4.2 and Table 4.3) were analyzed by SAXS in “as cast” and thermally annealed films. SAXS results are shown in Figure 4.23. All three mixed arm bottlebrush samples show distinct features in “as cast” films and features consistent with nanoscale ordering are also present in annealed films for P(75PDMS-co-25PLA)_{100} and P(25PDMS-co-75PLA)_{100}. All three mixed bottlebrush “as cast” films have nanoscale order along the \( q_z \) direction. Additionally P(25PDMS-co-75PLA)_{100} shows the strong appearance of a ring spreading from \( q_z \) to \( q_y \), indicating there are features approximately 24.15 nm (\( q = 0.026 \)) in size parallel and perpendicular to the film substrate. After annealing P(25PDMS-co-75PLA)_{100} the features become stronger in the \( q_y \) direction, indicating that there is preferential alignment perpendicular to the substrate.
Figure S4.15 SAXS data for mixed arm bottlebrushes $P(75\text{PDMS-co-25PLA})_{100}$, $P(50\text{PDMS-co-50PLA})_{100}$ and $P(25\text{PDMS-co-75PLA})_{100}$. Top row features untreated, as-cast films and bottom row shows SAXS data after thermal annealing. (Detector angle $\theta = 0.15$).

The temperature dependence of nanoscale features in mixed-arm bottlebrush copolymers was also studied by SAXS. SAXS results were obtained for all mixed-arm bottlebrush polymer films (as cast and annealed) at 45, 65, 85, and 120 °C. Temperature dependent SAXS data for $P(50\text{PDMS-co-50PLA})_{100}$ are shown in Figure 4.24. At room temperature ($T = 25^\circ\text{C}$), mixed bottlebrush polymer films show strong alignment in $q_z$ with features at $q = 0.026, 0.035, 0.072$ and $0.122$. Upon heating to 45 °C (close to the $T_g$ of PLA) ring features at higher $q_z$ disappear and new ordered features appear in $q_z$ 0.02, 0.024, 0.027, and 0.032 corresponding to 19.63 – 31.4 nm features. With further heating to 65 °C, the films are featureless and have no ordered structures. Above 45 °C the polymer are in the melt state and are not ordered. All mixed arm bottlebrush copolymers show increased features at 45 °C and feature-less SAXS results from 65 – 120 °C.
Blocky-type bottlebrush polymers with NB-PDMS and NB-PLA side-chains were prepared with varying molar block ratios of PDMS and PLA side-chains. Blocky bottlebrush polymers from NB-PDMS2k ($M_n$-$SC$ = 815 g/mol, $N_{SC-PDMS} = 35$) and NB-PLA2k ($M_n$-$SC$ = 600 g/mol, $N_{SC-PLA} = 33$) were prepared by sequential addition of macromonomers in ROMP polymerization. P(PDMS2k-$block$-PLA2k) bottlebrush polymers have molar % NB-PDMS2k $\phi$: 20, 40, 50, 60, and 80. Blocky bottlebrush polymers with 5k sidechains, P(PDMS5k-$block$-PLA5k), were also prepared by sequential ROMP of NB-PDMS2k ($M_n$-$SC$ = 240 g/mol, $N_{SC-PDMS} = 75$) and NB-PLA2k ($M_n$-$SC$ = 310 g/mol, $N_{SC-PLA} = 57$) macromonomers and have $\phi$: 20, 40, 50, 60, and 80. Films from bulk five P(PDMS2k-$block$-PLA2k) and five P(PDMS5k-$block$-PLA5k) bottlebrushes were cast at 20 mg/mL chloroform onto silicon wafers and measured by SAXS “as cast” or after 2 hours of thermal annealing (“Annealed” samples). SAXS results are shown in Figure 4.25 for P(PDMS2k-$block$-PLA2k) and Figure 4.26 for P(PDMS5k-$block$-PLA5k) films. We expected to observe the formation of lamellar features after annealing for these large blocky bottlebrushes, however there are no detectible nanoscale features in films for either molecular weight or $\phi$ value.
Figure S4.17 SAXS data from P(PDMS2k-block-PLA2k) with variations in PDMS molar content (φ) from 20 to 80 percent. Top row features untreated, as-cast films and bottom row shows SAXS data after thermal annealing. (Detector angle θ = 0.15).

Figure S4.18 SAXS data from P(PDMS5k-block-PLA5k) with variations in PDMS molar content (φ) from 20 to 80 percent. Top row features untreated, as-cast films and bottom row shows SAXS data after thermal annealing. (Detector angle θ = 0.15).
5. Biocompatible PLA-PEG bottlebrush copolymers and their self-assembly in water

5.1 Abstract

In this chapter we focus on biocompatible bottlebrush copolymers as drug delivery systems. Hydrophilic poly(ethylene glycol) (PEG) and hydrophobic poly(lactic acid) (PLA) are well-studied materials known to be biocompatible and PEG is also considered bioinert. We designed novel bottlebrush copolymers with PEG and PLA side-chains grafted to a poly(norbornene) backbone in two different design strategies: block copolymer side-chains (core-shell bottlebrush) and block copolymer backbone (blocky bottlebrush).

Core-shell bottlebrush polymers have a hydrophobic PLA core covalently bound to a PEG block that forms a water-soluble shell. This is a desirable conformation for drug encapsulation and release as the hydrophobic drug molecules can accumulate in the PLA core, while the PEG shell solvates the molecule and reduces phagocytosis in vivo. The core-shell bottlebrush polymers presented here have different PLA core sizes (PLA length 18 – 58, corresponding to $M_n$ 1 000 – 5 000 g mol$^{-1}$) and PEG coronas ($M_n$ 2 000 and 5 000 g mol$^{-1}$). The shape and size of core-shell polymers were studied by SANS analysis.

Blocky bottlebrush copolymers with block copolymer backbones have separate regions of PLA side-chains and PEG side-chains, forming a macromolecular brush block copolymer. Self-assembled structures of blocky bottlebrush polymers were formed by dialysis against water. Single particle size and shape were studied by DLS and SANS and found to be 10 – 12 nm in diameter and 21 – 39 nm long. Self-assembled blocky bottlebrush polymers were significantly larger in water. Spherical assemblies were observed by TEM, and the overall size was 200 – 375 nm. The internal structure of bottlebrush assemblies was investigated by SANS.
5.2 Introduction

Polymer systems are attractive as biological and chemical carriers. Advances in polymer chemistry allow precise control over final micro- and macroscopic properties, including size, molecular weight, solubility, toughness, size distribution, and supramolecular driving forces for assemblies. More recently, shape effects on biological processes have been studied. Distinct pharmacological effects have been noted for non-spherical polymer assemblies, including increased retention time\(^1\), enhanced targeting and novel flow patterns\(^2\). These preliminary studies have shown a strong dependence on shape with circulation time and phagocytosis. Long cylindrical shapes exhibited enhanced circulation half-lives as compared to short cylinders and spheres\(^1\).

Bottlebrush polymers represent a promising alternative to linear block copolymer assemblies because their size, shape, and conformation can be precisely controlled. Recent work has explored the use of bottlebrush polymers as controlled drug release vehicles\(^3\) and \textit{in vivo} imaging contrast agents\(^4\). The first example of bottlebrush polymer drug delivery was reported by Johnson et al. and employed elegant and complex chemistry yielding bivalent PEG macromonomers with covalently attached drug molecules\(^3\). In another study, self-assembled crosslinked bottlebrush polymer micelles were injected into the tail of tumor bearing mice in the first \textit{in vivo} study utilizing bottlebrush polymers for medical imaging contrast\(^4\). Short poly($\varepsilon$-caprolactone)(PCL)-\textit{block}-PEG bottlebrush polymers were loaded with DOX and presented release profiles of 120 hours, demonstrating successful incorporation of drugs in bottlebrush polymer structures\(^5\)\(^6\). Bottlebrush polymers have been used in micelle self-assemblies (D= 151-170nm)\(^4\). Bottlebrush polymers are capable of responding to stimuli, such as pH\(^7\)\(^9\) and temperature\(^10\). Stimuli responsive polymers offer another avenue for drug delivery and controlled release\(^11\). Here we are interested in designing biocompatible bottlebrush copolymers of novel, well-defined amphiphillic bottlebrush polymers with block copolymer sidechains and block copolymer backbones. The objective of this study is to develop novel bottlebrush copolymers for use as drug-delivery systems.

There have been several varied reports on bottlebrush copolymer synthesis. Often they involve the grafting-from approach, where side-chains are grown sequentially from the linear backbone or the macromonomer “grafting-through” approach. The latter method
allows for each side-chain polymer to be a di-block or tri-block copolymer or, by sequentially polymerizing various macromonomers, a blocky configuration along the backbone. Blocky bottlebrush polymers (bBBPs) by “grafting-through” are appealing as a fast (reaction times are typically less than 2 hours) and reliable (macromonomer conversions greater than 95%) approach. However, a one-pot method which utilized the various rates of reaction of each macromonomer is most appealing and has not been reported.

5.3 Material synthesis

5.3.1 Core-shell bottlebrush polymers

The synthesis of norbornene terminated PLA-\textit{block}-PEG macromonomers (NB-PLA-b-PEG) is shown in Scheme 5.1. We systematically varied the PLA “core” size by changing the molecular weight in the ring-opening polymerization discussed previously (REFER TO CHAPTER 2, Scheme 2.1). A representative synthesis of NB-PLA58-b-PEG5k is presented here. To a round bottom flask, Nb-PLA (0.50 g, 0.12 mmol), PEG-COOH (0.299 g, 0.06 mmol) and EDC (46 mg, 0.24 mmol) were combined with 5 mL of anhydrous dichloromethane and allowed to stir at RT until dissolved, followed by stirring for 30 minutes at 0 °C. DMAP (4.1 mg) was dissolved in 1 mL dichloromethane and added to flask dropwise. The reaction proceeded at RT for 48 hours. Product was isolated by diluting the organic phase with 10 mL DCM and washing with 0.1 M NaCl/DI water once and pure DI water twice. Organic phase was dried with MgSO$_4$ and concentrated in \textit{vacuo}. The final product NB-PLA-\textit{b}-PEG was confirmed by GPC and NMR characterization and is shown in Table 5.1. We varied the molecular weight of the PLA “core” block from 1 000 – 5 400 g mol$^{-1}$ and had either a 2k or 5k PEG corona.
Table 5.1. Properties of NB-PLA-b-PEG linear diblock macromonomers and resulting “core-shell” bottlebrush polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BCP Side-chain</th>
<th>Bottlebrush</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PLA</td>
<td>PEG</td>
</tr>
<tr>
<td>PNb(PLA18-PEG2k)$_{164}$</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>PNb(PLA34-PEG2k)$_{117}$</td>
<td>3000</td>
<td>2000</td>
</tr>
<tr>
<td>PNb(PLA48-PEG2k)$_{140}$</td>
<td>4000</td>
<td>2000</td>
</tr>
<tr>
<td>PNb(PLA58-PEG2k)$_{65}$</td>
<td>5400</td>
<td>2000</td>
</tr>
<tr>
<td>PNb(PLA58-PEG5k)$_{50}$</td>
<td>5400</td>
<td>5000</td>
</tr>
</tbody>
</table>
Scheme 5.1 Synthesis of NB-PLA-b-PEG diblock macromonomers and P(NB-PLA-b-PEG)$_m$ bottlebrush copolymers by EDC/DMAP coupling and ROMP polymerization. Where $m$ and $n$ represent the DP of PLA and PEG segments, respectively, and $X$ is representative of the bottlebrush polymer backbone DP.

Core-shell bottlebrush polymers were made by ROMP of NB-PLA-$b$-PEG diblock macromonomers with target backbone degree of polymerization (DP) 5 - 200. Resulting “core-shell” bottlebrush polymers and their properties are shown in Table 5.1. GPC traces for linear PLA-$b$-PEG2k macromonomers and bottlebrush polymers are shown in Figure 5.1. The core-shell polymer with PEG5k is shown separately in Figure 5.2.
Figure 5.1 GPC traces of NB-PLA-b-PEG linear diblock macromonomers and “core-shell” bottlebrush polymers synthesized by ROMP of linear macromonomers.
Figure 5.2 GPC traces of Nb-PLA58-PEG5k block copolymer and corresponding bottlebrush polymers PNb(PLA58-PEG5k).

5.3.2 Blocky bottlebrush copolymers

Poly(lactic acid)(PLA) and poly(ethylene glycol)(PEG) were selected as biocompatible, amphiphilic macromonomers, which can be readily synthesized. For this study we copolymerized NB-PLA2k ($M_n$ 2600 g mol$^{-1}$) and NB-PEG5k ($M_n$ 5300 g mol$^{-1}$). The synthesis of norbornene functionalized PEG (NB-PEG) is achieved by EDC/DMAP coupling of the alcohol terminated norbornene and monofunctional carboxylic acid PEG in dichloromethane for 24 hours. Synthesis and kinetics of norbornene functionalized PLA (NB-PLA) were previously reported by Xia, et al $^{12}$ and discussed in Chapter 2 of this doctoral thesis [Chapter 2, Scheme 2.1].
Figure 5.3 Synthesis of blocky PLA-PEG bottlebrush polymers by a “one-pot” ROMP of NB-PEG and NB-PLA. After dialysis from DMF to water, blocky bottlebrush copolymers self-assemble into large micelle structures (schematic, far right).

The homopolymer ROMP kinetics of each macromonomer were determined by sequentially removing aliquots of the bottlebrush synthesis reaction, immediately quenching with butyl vinyl ether, and determining mass ratio of remaining linear macromonomer and product $M_n$ and PDI. It is also important to consider the final conversion of NB-PLA and NB-PEG, which will affect the final composition of the bottlebrush polymer. In this study, NB-PLA has a slightly higher terminal conversion of 98% and NB-PEG is 95%. A linear regression is fit to a log-linear plot of macromonomer conversion and we find that the slope of NB-PLA2k is 1.08 and the slope of NB-PEG5k is 0.28. Comparing the slope of each macromonomer indicates that PLA macromonomers react 3.8 times faster than PEG. Therefore we expect a PLA-rich block followed by a PEG-rich block. Because identical norbornene end-groups were used, we are unable to monitor the relative rates of conversion during the polymerization by $^1$H NMR.
The steeper slope of NB-PLA macromonomers indicates a much faster reaction time, as compared to NB-PEG.

First, we synthesized two bBBPs with PLA and PEG side-chains by a “one-pot” method. Both macromomers were added to the same flask and dissolved in DCM. ROMP polymerization was initiated by the addition of Grubb’s second generation catalyst in a stock solution of DCM. After two hours the reactions were quenched by the addition of butyl vinyl ether. We varied the amount of NB-PLA and NB-PEG macromonomers for two samples. For \( P(\text{PLA}_{2k})_{25} - c - P(\text{PEG}_{5k})_{25} \) (mBBP1), we have a 1:1 ratio of NB-PLA2k and NB-PEG5k and a target backbone DP (ratio of macromonomer to catalyst) of 50. For \( P(\text{PLA}_{2k})_{50} - c - P(\text{PEG}_{5k})_{150} \) (mBBP2), we have a 1:3 ratio of NB-PLA2k to NB-PEG5k and a target backbone DP of 200. Bottlebrush copolymers prepared via a “one-pot” grafting-through polymerization have molecular weights 36.5 – 96.8 kg mol\(^{-1}\), molecular weight dispersities (PDI) less than 1.5, and macromonomer conversion 84 – 91 %.
Table 5.2 Properties of “blocky” bottlebrush polymers prepared via “one-pot” and sequential ROMP polymerization methods.

<table>
<thead>
<tr>
<th>Polymer Structure</th>
<th>Name</th>
<th>Synthesis</th>
<th>W%</th>
<th>PEG</th>
<th>$M_{n,PS}$</th>
<th>DP_BB</th>
<th>PDI</th>
<th>Conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(PLA2k)$<em>{25}$-c-P(PEG5k)$</em>{25}$</td>
<td>mBBP1</td>
<td>One-pot</td>
<td>50</td>
<td>36 500</td>
<td>50</td>
<td>1.16</td>
<td>91%</td>
<td></td>
</tr>
<tr>
<td>P(PLA2k)$<em>{50}$-c-P(PEG5k)$</em>{150}$</td>
<td>mBBP2</td>
<td>One-pot</td>
<td>75</td>
<td>96 800</td>
<td>200</td>
<td>1.42</td>
<td>84%</td>
<td></td>
</tr>
<tr>
<td>P(PLA2k)$<em>{100}$-b-P(PEG5k)$</em>{100}$</td>
<td>bBBP</td>
<td>sequential</td>
<td>50</td>
<td>75 800</td>
<td>200</td>
<td>1.23</td>
<td>90%</td>
<td></td>
</tr>
</tbody>
</table>

To compare the bottlebrush polymers made by “one-pot” polymerization with bottlebrush polymers known to have a block copolymer backbone, we prepared one blocky bottlebrush polymer by sequential addition of macromonomer side-chains. If the second macromonomer is added to the ROMP polymerization after complete consumption of the first macromonomer, the resulting bottlebrush is guaranteed to have a “blocky” structure. Referring again to the kinetic data shown in Figure 5.4, we observe that at 2 minutes, 99% of NBPLA macromonomers have been consumed. To prepare a blocky bottlebrush, we add Grubb’s catalyst to NB-PLA macromonomer solution, wait two minutes and then add NB-PEG macromonomers. A GPC aliquot prior to addition of NB-PEG confirmed that nearly 100% NB-PLA2k macromonomers reacted (green trace, Figure 5.5). This “sequential” polymerization method produced P(PLA2k)$_{100}$-b-P(PEG5k)$_{100}$ (bBBP) with a 1:1 ratio of NB-PLA2k to NB-PEG5k macromonomers with a target backbone DP of 200. The resulting bottlebrush has a molecular weight of 75 800 g mol$^{-1}$, PDI of 1.23 and 90% macromonomer conversion.
Figure 5.5 GPC traces during ROMP polymerization of “blocky” bottlebrush polymer via a sequential addition of macromonomer method. The final bottlebrush copolymer (black trace) has unreacted PEG macromonomer.

Self-assemblies from mBBP-1, mBBP-2, and bBBP were prepared by dissolving 10 mg/mL polymer in DMF, followed by dialysis against DI water for 24 hours. The resulting assemblies were first confirmed by dynamic light scattering, which confirmed the presence of large > 200 nm structures in water. Samples prepared by “one-pot” and “sequential addition” synthesis methods show similar patterns in DLS results. DLS provides valuable bulk size distribution data but cannot indicate the shape of the structures.

Figure 5.6 Dynamic light scattering (DLS) size distributions of blocky bottlebrush copolymers as single particles in organic solvents (red bars) and after dialysis into water
(blue bars), showing at least one order of magnitude increase in size. Blocky bottlebrush polymer samples: A) P(PLA2k)25-c-P(PEG5k)25, B) P(PLA2k)50-c-P(PEG5k)150, and C) P(PLA2k)100-b-P(PEG5k)100.

5.4 Characterization by Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) is a powerful characterization technique that is capable of determining overall size and shape (form factors) of organic nanoparticles, including bottlebrush polymers\textsuperscript{13-17}. Small-angle neutron scattering experiments were carried out at NIST to characterize the absolute size and morphology of core-shell bottlebrush polymers in organic solvents (methanol and toluene) and aqueous environments. We performed solution SANS measurements on the single bottlebrush polymers in 1 wt\% organic solvent and the bottlebrush assemblies after dialysis against D\textsubscript{2}O. SANS results are shown in Figures 5.7 and 5.8. In dioxane, all bottlebrush copolymers have some aggregates present, as evident by the upturn in low-\(q\). The single molecule form factor is observed in the middle-\(q\) region (0.0004 < \(q\) < 0.007). The plateau region will be fit to a Guinier-Porod and cylinder model to deduce the polymer size in solution. After dialysis against water, we clearly observe the appearance of large, ordered structures in the SANS data by the appearance of high intensity features at low \(q\) \((q < 0.005)\) in all cases. The single-molecule form factor is still visible because SANS probes multiple length scales simultaneously (this does not indicate that both single-molecules and aggregates are present, however it cannot prove the absence of single particles).

5.4.1 Core-shell bottlebrush polymers

We expected a larger overall size for core-shell bottlebrushes in organic solvents as the polymer side-chains should swell in good solvent conditions. Core-shell bottlebrush polymers did not directly dissolve in water; therefore dialysis from a methanol solution was required to get bottlebrushes in water. Scatter profiles for all core-shell bottlebrush polymers are shown in Figure 5.7. Methanol is a good solvent for PEG and a poor solvent for PLA. The SANS scatter patterns shown in Figure 5.7 (left) reveal that three
core-shell polymers dissolve directly in methanol (PNb(PLA18-PEG2k)_{164}, PNb(PLA34-PEG2k)_{117}, and PNb(PLA58-PEG5k)_{50}) whereas the other two samples have no observable scattered intensity indicating that the polymers are not in present in solution. From these results we conclude that good methanol solubility with 2k PEG is achieved with PLA cores with $M_n$ 3000 g/mol (DP = 34) or less and for a 5k PEG good solubility is observed for PLA core of $M_n$ 5 000 g/mol. When the PLA block is longer, the core-shell polymer precipitates in methanol. All other core-shell bottlebrush polymers precipitated from water, except PNb(PLA18-PEG2k)_{164} which stayed in solution but was strongly aggregated.

![Figure 5.7](image)

**Figure 5.7** SANS scatter profiles for core-shell bottlebrush polymers in methanol-$D_4$ (left) and SANS results for PNb(PLA58-PEG5k)_{50} in toluene-$D_8$ (red), methanol-$D_4$ (green) and water-$D_2O$ (blue) (right). The peak at $q \sim 0.06$ indicates that after dialysis PNb(PLA58-PEG5k)_{50} restructures and forms a defined interface between the PLA core and flexible PEG corona.

First we apply a Guinier-Porod model to core-shell bottlebrushes in methanol-$D_4$. Results are shown in Table 5.3. Only PNb(PLA18-PEG2k)_{164} and PNb(PLA34-PEG2k)_{117} fit the Guinier-Porod model well. PNb(PLA58-PEG5k)_{50} returned a negative value for $s$ and therefore the results are unreliable. Polymers that did not dissolve were not analyzed. Next, we applied a core-shell cylinder model to PNb(PLA58-PEG5k)_{50} in methanol and water (after dialysis). The core-radius, $R_{core}$, decreases in water as
compared to methanol from 54.8 ± 0.1 Å to 48.8 ± 0.2 Å. The overall radius of particles also decreases in water from 70.4 ± 0.1 Å to 62.5 ± 0.1 Å. The bottlebrushes also have a decreased length in water from 272 ± 0.6 Å to 224 ± 0.7 Å. Overall the particles appear to become more compact in water and the PLA core has a harder, more ordered interface after dialysis in water.

Table 5.3 Fitted results for core-shell bottlebrush polymer SANS data from Guinier-Porod and core-shell cylinder models.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>( R_g [\text{Å}] )</th>
<th>( s )</th>
<th>Porod exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb(PLA18-PEG2k)(_{164})</td>
<td>MeOH</td>
<td>37</td>
<td>0.19</td>
<td>2.9</td>
</tr>
<tr>
<td>PNb(PLA34-PEG2k)(_{117})</td>
<td>MeOH</td>
<td>60</td>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>PNb(PLA58-PEG5k)(_{50})</td>
<td>MeOH</td>
<td>122*</td>
<td>-2.3*</td>
<td>5.4*</td>
</tr>
</tbody>
</table>

Core-shell Cylinder Model

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( R_{\text{core}} )</th>
<th>( R_{\text{total}} )</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNb(PLA58-PEG5k)(_{50})</td>
<td>MeOH</td>
<td>54.8 ± 0.1 Å</td>
<td>70.4 ± 0.1 Å</td>
</tr>
<tr>
<td>PNb(PLA58-PEG5k)(_{50})</td>
<td>D(_2)O</td>
<td>48.8 ± 0.2 Å</td>
<td>62.5 ± 0.1 Å</td>
</tr>
</tbody>
</table>

* Value for \( s \) is negative and far from 0, therefore the Guinier-Porod model does not approximate the particle well.

SANS results are fit to three models for analysis: Guinier-Porod\(^\text{18}\), cylinder and core-shell cylinder. Detailed explanations of each model can be found in Chapter 1. First, the Guinier-Porod model is used to predict a shape by fitting the \( S \) parameter. When \( S = 0 \), the particles are spheres and as \( S \) approaches 1, the polymers become more elongated. From the results presented in Table 5.3, P(PLA2k)\(_{25}\)-c-P(PEG5k)\(_{25}\) and P(PLA2k)\(_{50}\)-c-P(PEG5k)\(_{150}\) are close to spherical particles and P(PLA2k)\(_{100}\)-b-P(PEG5k)\(_{100}\) is much more elongated (\( S = 0.75 \)). Next, we fit the scatter profiles to a cylinder model to determine the radius (\( R_{\text{cyl}} \) ) and length (\( L_{\text{cyl}} \)) of single bottlebrush polymers. We expect variance in radius between samples as there are varying fractions of NB-PEG5k
macromonomer, which has a higher side-chain DP (therefore longer cross-section). Radii for blocky bottlebrush polymers are 50.0 to 58.1 Å or 10 – 12 nm in diameter. The fitted length of bottlebrush polymers varies more than expected in the series. Bottlebrush length should increase with backbone DP, however of the two samples with backbone DP = 100, P(PLA2k)_{100-b}-P(PEG5k)_{100} has a longer fitted length of 390 Å compared to 256 Å for P(PLA2k)_{50-c}-P(PEG5k)_{150}.

The size and detailed structural information for the self-assembled structures of bottlebrush polymers in water could not be deduced by applying models to the SANS data because we have a limited q-range. To obtain information about the overall size, we would need to have the region of scatter data in which the plateau region exists, which would be at lower q angles that are measured here. However, we can apply the Guinier-Porod model to the middle q region to obtain conformational information about how the individual bottlebrushes pack within the aggregate structures. We focus our attention on the radius of gyration, \( R_g \), and notice that polymers with 1:1 ratio of NB-PLA: NB-PEG side-chains (P(PLA2k)_{25-c}-P(PEG5k)_{25} and P(PLA2k)_{100-b}-P(PEG5k)_{100}) have similar fitted \( R_g \) values in the aggregate as we observe in single molecular arrangement (\( R_{cyl} \)). The \( R_g \) for P(PLA2k)_{50-c}-P(PEG5k)_{150} is much lower than the fitted \( R_{cyl} \) value. This may indicate that the bottlebrush polymer with 75% PEG side-chains collapses within the aggregate structure. However, this should be interpreted with caution because this model may not be appropriate for fitting polymers within a self-assembled structure.
Figure 5.8 Small-angle neutron scattering (SANS) characteristic scatter traces for individual blocky bottlebrush polymers dissolved in 1,4 dioxane-\textit{D}8 (red) or methanol-\textit{D}4 (green) and as large self-assembled structures in water-\textit{D}2\textit{O} (blue) for P(PLA2\textit{k})_{25-c-P(PEG5\textit{k})}_{25} (top), P(PLA2\textit{k})_{50-c-P(PEG5\textit{k})}_{150} (middle) and P(PLA2\textit{k})_{100-b-P(PEG5\textit{k})}_{100} (bottom). Representative TEM images of bottlebrush assemblies are shown in the right column. Scale bar100 nm.
Table 5.3 Fitted results for SANS data from blocky bottlebrush polymers in organic solutions (single particle form factors) and bottlebrush assemblies in water.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$S$</th>
<th>$R_{cyt} [\text{Å}]$</th>
<th>$L_{cyl} [\text{Å}]$</th>
<th>$S_{\text{polymer}}$</th>
<th>$R_g [\text{Å}]$</th>
<th>$v_{\text{aggregate}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mBBP1</td>
<td>0.02 ± 0.01</td>
<td>50.0 ± 0.1</td>
<td>214 ± 1.7</td>
<td>0.0 ± 0.01</td>
<td>68.3 ± 0.4</td>
<td>2.4 ± 0.3</td>
</tr>
<tr>
<td>mBBP2</td>
<td>0.19 ± 0.01</td>
<td>50.7 ± 0.1</td>
<td>256 ± 2.5</td>
<td>2.3 ± 0.04</td>
<td>26.6 ± 1.3</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>bBBP</td>
<td>0.75 ± 0.01</td>
<td>58.1 ± 0.1</td>
<td>390 ± 7.6</td>
<td>0.9 ± 0.01</td>
<td>50.5 ± 0.5</td>
<td>2.1 ± 0.0</td>
</tr>
</tbody>
</table>

To confirm the shape and size of the aggregates, we performed TEM on all samples. Representative TEM images of all aggregates are shown in Figure 5.8. In all cases, we observe large, spherical structures, between 200 – 375 nm, consistent with the formation of micelles. Although the aggregates are expected to shrink from dehydration, the shape of the self-assembled structures will remain intact. Furthermore, the size obtained from TEM is in good agreement with DLS, indicating that dehydration did not affect the particles greatly. Interestingly, the particle size did not vary significantly from sample to sample, indicating that the “one-pot” bottlebrush polymers are behaving identical to the confirmed bBBP samples. This further supports our conclusion that the kinetic differences of NB-PEG and NB-PLA are great enough to produce a nearly blocky bottlebrush polymer in a “one-pot” reaction vessel.

5.5 Conclusion

Biocompatible bottlebrush copolymers consisting of poly(lactic acid)(PLA) and poly(ethylene glycol) (PEG) were prepared with block copolymer side-chains (core-shell bottlebrushes) and block copolymer backbones (blocky bottlebrushes). Core-shell bottlebrush polymers with PLA core lengths $N_{SC}$ 18 – 58 and PEG coronas of $M_n$ 2 000 or 5 000 g mol$^{-1}$ were studied by SANS. Core-shell bottlebrush polymers did not directly dissolve in water, therefore dialysis from a methanol solution was utilized to achieve suspension in water. SANS results on core-shell bottlebrush polymers show the PEG block length must be of equal or greater length (molecular weight) than the PLA segment to be able to sufficiently dissolve in methanol. Next, we studied the size of individual
blocky PNb(PLA)-block-PNb(PEG2k) bottlebrush polymers and their self-assembled structures by SANS, DLS, and TEM. Blocky polymers made by a “one-pot” method, which takes advantages of large differences in the macromonomer ROMP kinetics, and “sequential addition” method both generate large, spherical micelle-like structures in water. The individual blocky bottlebrushes are 20 – 40 nm long (SANS measurements) and the spherical assemblies are 200 – 375 nm (TEM). SANS, DLS, and TEM measurements are in good agreement and support formation of large spherical blocky bottlebrush micelles in water. These large, tailored nanoparticle assemblies are strong candidates for future drug-encapsulation and release studies owing to their biocompatible materials and ideal size range for drug delivery systems.

5.6 References


6. Future Outlook and Applications of Bottlebrush Polymers

6.1 Abstract

The work reported in this chapter discusses preliminary data for two ongoing projects that demonstrate the potential future directions for applications of bottlebrush polymers. First we will discuss bottlebrush polymers as additives in polymer nanocomposite systems to modify thermal properties. Polymer nanocomposites (PNCs) are prepared by adding nanoparticles to a polymer matrix, and the addition of nanoparticles can influence mechanical and thermal properties. Bottlebrush polymers can similarly function as additives to tune mechanical and thermal properties, and we investigate whether models applicable to nanoparticle composites can also be used with polymer-bottlebrush blends. We prepare blends of linear polymer with added bottlebrush and measure changes in the glass transition temperature $T_g$. This is compared with a quantitative theory for changes in the glass-transition temperature based on the different surface energies of additive and linear polymers. We find good agreement between the model and experimental measurements in some cases, and in other cases our experimental results do not show a trend.

In a very different application, we are interested in the potential antifouling properties of bottlebrush polymers with hydrophilic side-chains. Polymer brush coated surfaces have been shown to reduce surface fouling, but the preparation of polymer brushes over large areas is impractical. Bottlebrush polymers can be synthesized in a batch reaction and deposited on a surface using conventional solution processing techniques, resulting in a brush-like film coating. The antifouling properties of bottlebrush coatings have not been previously reported. Here, we specifically propose to investigate bottlebrush polymers with poly($N$-isopropyl acrylamide) (PNIPAAm) side-chains. PNIPAAm has been shown to have antifouling properties, and here we propose to compare the
antifouling properties of bottlebrushes with linear polymers and investigate the roles of side-chain length, backbone length, and temperature. Our work will include comparing cell attachment to crosslinked PNIPAAm bottlebrush films with polymer film standards, such as hydrophobic polystyrene films. The temperature dependent release of attached cells will be evaluated by attaching cells at $T < T_{LCST}$ when NIPAAm films are swollen and heating the samples to $T > T_{LCST}$, where bottlebrush films are expected to contract and expel the biomass from the films. Preliminary results indicate that PNIPAAm bottlebrush films exhibit lower cell attachment than linear PNIPAAm and linear polystyrene films.

6.2 Bottlebrush Blends

6.2.1 Introduction

Polymer nanocomposites (PNCs) are a class of materials that are prepared by blending nanoparticles with a polymer host. The addition of nanoparticles can result in significant changes in the physical properties of the resulting PNC due to interfacial interactions that occur between polymer chains and the polymer surface. Attractive polymer-nanoparticle interactions generally result in an increase in the glass-transition temperature $T_g$, up to 10 - 40 °C for carbon (graphene and graphite derivatives)\textsuperscript{1-4} and silica\textsuperscript{5} nanomaterial fillers. Repulsive interactions generally produce a decrease in the $T_g$, up to 20 °C in PNCs with aluminum\textsuperscript{6} and silica\textsuperscript{7,8} nanoparticles. Recently reported systems with polymer-grafted nanoparticles have reported more modest changes in $T_g$ of up to 10 °C\textsuperscript{9-11}. These effects can be attributed to changes in the polymer dynamics near the nanoparticle surface, and as a result the nanoparticle concentration and inter-particle spacing also influence the glass-transition temperature\textsuperscript{5,9}. Decreased particle spacing (either from a higher nanoparticle concentration or better nanoparticle dispersion) produces greater surface interactions and as a result in larger changes in $T_g$. If the nanoparticle aggregates within the host polymer, the interparticle spacing increases, the interaction between the host polymer and nanoparticle decreases (less exposed surface energy) and the observed change in $T_g$ is decreased\textsuperscript{5,7,9}.
Here, we aim to investigate bottlebrushes as additives and investigate their impact on the physical properties of linear polymer matrices. We apply a model developed by Natarajan et al. which makes quantitative predictions in the change of $T_g$ for polymer nanocomposites given the polar and dispersive surface energies of the host polymer and the additive (filler) material as well as the inter-particle spacing. First, surface energies of all polymers are determined by contact angle measurements from water, formamide and diiodomethane. These values are used to predict a qualitative change in $T_g$ for our polymer-bottlebrush PNCs. Bottlebrush polymers are assumed to be well-dispersed in all cases. Next we compare the predictions from the model to experimental changes in $T_g$ measured from polymer-bottlebrush blends with 1 – 40 wt% bottlebrush additive.

6.2.2 Experimental

6.2.2.1 Materials

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used as received. Lactide was purchased from Sigma-Aldrich and recrystallized from ethyl acetate twice prior to use. Norbornenyl alcohol was modified from a previous report$^{12}$. Anhydrous dichloromethane (DCM) was purchased from Sigma-Aldrich and degassed prior to use. Modified Grubb’s catalyst ((H$_2$IMes)(pyr)$_2$(Cl)$_2$RuCHPh) was synthesized as previously described$^{13}$. Polystyrene ($M_n$ 150, 000 g/mol) was purchased from Sigma-Aldrich. Poly(methyl methacrylate) (PMMA) ($M_n$ 550, 000 g/mol) was purchased from Alfa Aesar.

**Synthesis of norbornene-poly(D,L-Lactic acid) (Nb-PLA).** NB-PLA$_{51}$ was synthesized via ring opening polymerization in the presence of stannous octoate and a norbornenyl-alcohol, modified from a previous report$^{12}$. In a representative reaction lactide (4.9 g, 33.78 mmol), N-(Hydroxypentanyl)-cis-5-norbornene-exo-2,3-dicarboximide (Nb-OH) (0.601 g, 2.41 mmol) and stannous octoate (35.4 mg, 0.088 mmol) reacted for 19 hours at 120°C. The polymer was collected by precipitation in methanol to yield NbPLA$_{51}$ ($M_n$ 3609 g mol$^{-1}$ PDI 1.45, yield 2.85 g (58 %)).

**Synthesis of PLA bottlebrush polymers (PNb(PLA)$_{51}$)$_{100}$.** Ring-opening metathesis polymerization (ROMP) of the terminal norbornene affords bottlebrush polymers with
polynorbornene backbones and PLA side-chains. Slightly modified from our previous report, macromonomer Nb-PLA51 (0.1 g, 0.28 mmol) was added to a 5mL round bottom flask equipped with a stir bar. The flask was vacuum dried and backfilled with nitrogen three times, followed by the addition of DCM (0.05 M). A stock solution of Grubb’s catalyst (0.01 g in 1.0 mL DCM) was added to the macromonomer solution at specified molar ratios. After two hours, the reaction is quenched by addition of butyl vinyl ether (0.1 mL) followed by precipitation in 100 mL cold methanol. PNb(PLA51)_{100} Mn 121 600 g mol\(^{-1}\), PDI 1.21, yield 132.43 mg (80 %).

**Film preparation.** All films were cast on cleaned silica wafers. Wafers cleaned by sonication in 2 wt% soap solution in water, DI water, and isopropyl alcohol for 30 minutes per solvent. After drying, polymer solutions (20 mg mL\(^{-1}\) in chloroform) were spin casted for 60 s at 1500 rpm and 30 s at 300 rpm, typically producing films ~100 nm.

**Polymer blend procedure.** Bulk polymer solutions of bottlebrush polymer are prepared at 5 mg/mL and solutions of host polymer were prepared at 50 mg/mL in chloroform. Blends at the desired weight fraction (1, 5, 10, 20 and 40 wt%) were prepared in solution by addition of bottlebrush and host polymer solutions to the desired ratios. Blend solutions were precipitated from methanol (poor solvent for host and bottlebrush polymer) *in situ* and collected from the vial, dried *in vacuo* 48 – 72 hours and weighed. Dried powder from polymer blends was collected and analyzed by DSC.

### 6.2.2.2 Instrumentation

**Gel-Permeation Chromatography (GPC).** Polymer molecular weights and molecular weight dispersities were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10000 Å pore sizes), an Agilent variable wavelength UV/vis detector, a Wyatt technology HELEOS II multiangle laser light scattering (MALLS) detector (\(\lambda = 658\) nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/vis (SEC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer \(dn/dc\) values were calculated
assuming 100% mass recovery and correcting the injected mass to account for unreacted macromonomer.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Proton-NMR (1H NMR) spectra were recorded using tetramethylsilane as internal standard in CDCl₃ on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm o.d. tubes with the concentration of 10 mg/mL.

**Differential Scanning Calorimetry (DSC).** DSC measurements were performed on TA Instruments DSC Q20 series. Polymer samples (2 – 5 mg) were placed in hermetically sealed aluminum DSC pans purchased from Thermal Support. For PS blends, samples were heated from 50 °C to 150 °C at 5°C/minute, held isothermal for 5 minutes, and cooled back to 50 °C at -5 °C/minute per cycle. For PMMA blends, samples were heated from 25°C to 250 °C at 5°C/minute, held isothermal for 5 minutes, and cooled back to 25 °C at -5 °C/minute per cycle. A total of three cycles were run per sample and Tₛ values were taken from the second cycle.

**Contact Angle goniometry.** Static contact angle measurements of water, formamide and diiodomethane on polymer films were carried out using a Drop Shape Analyzer DSA 100 (Kruss Instruments) at ambient conditions. Contact angles were recorded every 0.5 s for 120 seconds after drop deposition. Equilibrium contact angles were taken to be the average value over at least 20 seconds of stable CA value. Measurements were repeated at least on three different locations per substrate per sample per fluid. The final reported values represent an average and standard deviation of each film.

6.2.3 Results

6.2.3.1 Surface Energy of Polymer Films

To predict the change in thermal properties of bottlebrush blends in linear polymer matrices, we first need to determine the polar and dispersive surface energies of each blend component (bottlebrush and linear polymers). We prepared films of P(Nb(PLA51))₁₀₀ bottlebrush, linear polystyrene (PS) and linear poly(methyl methacrylate) (PMMA) by spin-casting polymer solutions (20 mg/mL in CHCl₃) onto freshly prepared
silicon wafers. For each polymer type, contact angle values were determined from three test fluids: water (H₂O), formamide (CH₃NO), and diiodomethane (CH₂I₂). Contact angle values (θ) from the three liquids are used to calculate the polar and dispersive surface free energies for each polymer by the following equation:

\[(1 + \cos \theta) \gamma_L = 2 \sqrt{\gamma_S^d \gamma_L^d} + 2 \sqrt{\gamma_S^p \gamma_L^p} \quad \text{(Eqn. 6.1)}\]

Where \(\theta\) is the contact angle between the solid and liquid, \(\gamma_L\) is the total surface free energy for the liquid, \(\gamma_S^d\) and \(\gamma_L^d\) are the dispersive surface energies, and \(\gamma_S^p\) and \(\gamma_L^p\) are the polar surface energies for the solid and liquid, respectively. The system of equations can be solved with only two liquids; therefore the surface energy values reported are taken by the average of three solvent combinations.

Contact angle results and surface energy calculations for the polymers studied here are presented in Table 6.1. Reported surface energy values for PMMA (\(\gamma = 40.2\) mJ/m²) are in good agreement with our results and calculated surface energy for PS (\(\gamma = 42\) mJ/m²) also falls within reported literature values\(^{15}\). The surface free energy of bottlebrush PNb(PLA51)\(_{100}\) \(\gamma_F = 34.70\) falls between the calculated surface energy for PMMA (\(\gamma_p = 40.27\) mJ/m²) and PS (\(\gamma_p = 29.36\) mJ/m²).
Table 6.1 Measured contact angle results and calculated surface energy values for bottlebrush PNb(PLA51)\textsubscript{100}, PS and PMMA polymer films.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Contact Angle (°)</th>
<th>Surface Energy (mJ/m\textsuperscript{2})</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H\textsubscript{2}O</td>
<td>CH\textsubscript{3}NO</td>
<td>CH\textsubscript{2}I\textsubscript{2}</td>
<td>Polar, $\gamma^p$</td>
</tr>
<tr>
<td>PNb(PLA51)</td>
<td>79.4 ± 0.6</td>
<td>60.3 ± 2.0</td>
<td>56.3 ± 0.7</td>
<td>5.81</td>
</tr>
<tr>
<td>PS</td>
<td>89.0 ± 0.7</td>
<td>78.4 ± 0.4</td>
<td>32.3 ± 0.5</td>
<td>3.60</td>
</tr>
<tr>
<td>PMMA</td>
<td>74.5 ± 0.6</td>
<td>60.3 ± 0.5</td>
<td>36.6 ± 0.8</td>
<td>6.05</td>
</tr>
</tbody>
</table>

6.2.3.2 Predicting changes in glass transition temperature

Using an in-house developed Matlab code (included in Section 6.6 Supplemental Information) based on the equations presented by Natarajan et al\textsuperscript{9}, we qualitatively predict the directional change in glass transition temperature for bottlebrush-polymer blends. We briefly explain the hypothesis presented by Natarajan et al here. Recall that changes in thermal properties for PNCs are determined by the attractive/repulsive interactions between polymer and filler and the filler’s interparticle spacing. The attractive/repulsive interactions are predicted by the ratio of the work of adhesion between the filler and polymer to the work of adhesion between polymer-polymer interactions ($W_{FP}/W_{PP}$). These interactions can be determined by the hypothetical wetting contact angle of the filler onto the surface of the polymer. Experimentally measuring this contact angle is infeasible because both host polymer and filler are solid. Referring to Equation 6.1 this polymer-polymer contact angle can be approximated if the polar and dispersive surface energies for filler and polymer are known. Conceptually, if the filler “wets” the polymer (ie. has a small contact angle) the filler will be well dispersed in the polymer due to positive polymer-filler interactions and $W_{FP}/W_{PP}$ is greater than or equal to 1. Iso-contact angle lines (shown in blue in Figures 6.1 – 6.2) represent solving
equation 6.1 for $\theta = 0^\circ, 30^\circ,$ and $45^\circ$. The envelope inside Iso-Contact angle = $0^\circ$ represents complete wetting. Work of adhesion, $W_a$, represents the driving force for filler aggregation. Larger $\Delta W_a$ indicates a larger driving force for filler aggregation, but this effect will not be studied here. Lastly, work of spreading, $W_s$, relates to polymer chain mobility and the attraction of the filler to the host polymer surface. Iso-$W_s$ lines graphically represent the surface energies correlating to attractive (positive $W_s$) and nonattractive (zero or negative $W_s$) forces between filler and polymer. This is represented graphically by an iso-work of spreading (iso-$W_s$) line. Importantly for our study, when output point for the bottlebrush polymer falls below the iso-$W_s = 0$ line, we expect a decrease in host polymer $T_g$. Similarly, if the bottlebrush point falls above iso-$W_s = 0$ line, we expect an increase in measured host polymer $T_g$.

Using the calculated polar and dispersive surface energies for the host polymer and bottlebrush filler shown in Table 6.1, we make theoretical predictions for the directional changes in host polymer $T_g$. Figure 6.1 shows the prediction for bottlebrush/PS blends and Figure 6.2 shows the prediction for bottlebrush/PMMA blends. For bottlebrush/PS blends the bottlebrush filler lies above the iso-$W_s = 5$ line, therefore we expect an increase in PNC $T_g$ with increasing bottlebrush additive. Conversely, for the bottlebrush/PMMA blends the bottlebrush filler output lies below iso-$W_s = -5$ line, therefore we expect a decrease in PNC $T_g$. 

Figure 6.1 Graphical representation of the bottlebrush/PS blends showing iso-contact angle, iso-$W_a$ and iso-$W_s$ lines. Bottlebrush output lies close to iso-$W_s = 5$ line, therefore we expect an increase in polymer blend $T_g$. 
Figure 6.2  Graphical representation of the bottlebrush/PMMA blends showing iso-contact angle, iso-$W_a$ and iso-$W_s$ lines. Bottlebrush output lies below the iso-$W_s = -5$ line, therefore we expect a decrease in polymer blend $T_g$.

6.2.3.3 Experimental $T_g$ results for bottlebrush/polymer blends

Blends of host polymer (PS or PMMA) and bottlebrush polymer were prepared at 1, 5, 10, 20, and 40 wt % bottlebrush additive by solution blending and precipitating polymer blends from poor solvents. Blends were dried in vacuo for a minimum of 48 hours prior to DSC sample preparation. Thermal properties were characterized by DSC experiments and are shown in Table 6.2 and Figure 6.3. For bottlebrush blends in PS, the $T_g$ increases with larger amounts of PLA bottlebrush polymers from 104.9 °C for pure PS to up to 111.9 °C for 40 wt% blends. This increasing trend is in agreement with the theoretical prediction. For bottlebrush blends in PMMA, the $T_g$ decreases with bottlebrush additives from 125.6 °C for pure PMMA to 122.3 °C for 20 wt% blends. The 40 wt% blend of
bottlebrush-PMMA did not show a glass transition. The decreasing trend in $T_g$ for bottlebrush-PMMA blends is in agreement with theoretical predictions.

**Table 6.2** DSC results for bottlebrush-polymer blends with calculated mass fractions shown.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Mass BB (mg)</th>
<th>Mass PS (mg)</th>
<th>wt % BB</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td>0.00</td>
<td>104.91</td>
</tr>
<tr>
<td>1% BB in PS</td>
<td>0.52</td>
<td>49.14</td>
<td>1.04</td>
<td>105.88</td>
</tr>
<tr>
<td>5% BB in PS</td>
<td>2.51</td>
<td>47.11</td>
<td>5.06</td>
<td>106.82</td>
</tr>
<tr>
<td>10% BB in PS</td>
<td>1.95</td>
<td>17.74</td>
<td>9.91</td>
<td>107.06</td>
</tr>
<tr>
<td>20% BB in PS</td>
<td>3.94</td>
<td>15.77</td>
<td>20.00</td>
<td>107.55</td>
</tr>
<tr>
<td>40% BB in PS</td>
<td>7.56</td>
<td>11.88</td>
<td>38.91</td>
<td>111.88</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td></td>
<td>0.00</td>
<td>125.62</td>
</tr>
<tr>
<td>1% BB in PMMA</td>
<td>0.53</td>
<td>49.75</td>
<td>1.05</td>
<td>127.41</td>
</tr>
<tr>
<td>5% BB in PMMA</td>
<td>2.50</td>
<td>47.88</td>
<td>4.96</td>
<td>125.89</td>
</tr>
<tr>
<td>10% BB in PMMA</td>
<td>5.07</td>
<td>44.73</td>
<td>10.17</td>
<td>124.11</td>
</tr>
<tr>
<td>20% BB in PMMA</td>
<td>5.98</td>
<td>24.57</td>
<td>19.58</td>
<td>122.33</td>
</tr>
<tr>
<td>40% BB in PMMA</td>
<td>7.25</td>
<td>11.16</td>
<td>39.40</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure 6.3 Change in $T_g$ of bottlebrush blends with respect to pure host polymer $T_g$. The $T_g$ of bottlebrush blends in PS increase with added bottlebrush and decrease for blends in PMMA.

6.2.4 Conclusion and Future Direction

Changes in thermal properties of bottlebrush polymer blends in a host polymer can be predicted based on surface energy differences as described by Natarajan et al. Poly(lactic acid) bottlebrush polymers were blended with linear polystyrene and poly(methyl methacrylate) hosts at 1, 5, 10, 20 and 40 wt% additive. The surface energies of each polymer component were determined by contact angle measurements and used as inputs for the theoretical model. Based on Natarajan’s hypothesis, PLA bottlebrush blends with PS should increase the $T_g$ with respect to the bulk PS matrix and PLA bottlebrush blends with PMMA should decrease the $T_g$. Experimental DSC results for 1 – 40 wt% are in agreement with these predictions.

We have also measured the $T_g$ for blends of PNb(PLA51)$_{100}$ bottlebrush polymers with poly(tert-butyl acrylate) (PtBA) and poly(vinyl piridole) (PVP). After experimenting with several processing techniques for PtBA blends, including precipitation solvents, vacuum drying under elevated temperatures and drying times, we were still unable to
measure a reliable glass transition temperature. Therefore this system was abandoned. The current challenge for blends with PVP as the host polymer are in determining the surface energies of PVP. Because PVP is very hydrophilic, we were unable to determine the contact angle of the polymer films for any solvent. Finally, we have also explored measuring the change in \( T_g \) with different bottlebrush polymer types (change the side-chain polymer) and lengths. Polymer blends with PLA bottlebrushes with shorter backbone lengths (PNb(PLA51)\(_{20}\)) did not show a trend in \( T_g \) with increasing bottlebrush additive. Ongoing work is exploring blends with polystyrene bottlebrush, PNb(PS-3k)\(_{100}\) with linear PS and PMMA. We expect these blends to be a reliable system to study the changes in thermal properties in bottlebrush blends.

6.3 Anti-biofouling coatings with PNb(PNIPAAm) bottlebrushes

6.3.1 Introduction

Polymer brushes have been extensively studied for anti-fouling applications, owing their improved resistance to biological fouling moieties to the flexible chains extending from the brush layer. However, polymer brushes are impractical to coat large surfaces due to the chemistry required to prepare polymer brushes. Bottlebrush polymers could be prepared separately, dissolved in solution and spray-coated in large quantities, also resulting in a brush-like layer at the coating surface. Ongoing work in our laboratory focuses on preparing crosslinkable PNIPAAm bottlebrush films that are stable for long periods in time in aqueous environment. Preliminary temperature dependent cell attachment studies with these films showed decreased cell attachment at low temperatures as compared to films from linear polymers.

6.3.2 Experimental

6.3.2.1 Materials

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used as received. Modified Grubb’s catalyst ((H\(_2\))IMes)(pyr)\(_2\)(Cl)\(_2\)RuCHPh) was synthesized as previously described\(^{13}\). N-isopropylacrylamide (Aldrich, 97%) was
purified by recrystallization in hexane for three times. 2,2′-azobis(2-methylpropionitrile) (AIBN) was purified by recrystallization in methanol. Modified Grubb’s catalyst ((H2IMes)(pyr)2(Cl)2RuCHPh)13. exo-7-Oxabicyclo- [2.2.1]hept-5-ene-2,3-dicarboxylic anhydride16, norbornene-functionalized chain transfer agent (NB-CTA) N- (pentynoyl-2-(dodecylthiocarbonothioylthio)-2-methylpropanyl)-cis-5-norbornene-exo-2,3-dicarboximide14, were synthesized as previously reported. Anhydrous dichloromethane (DCM) was purchased from Sigma-Aldrich and degassed prior to use.

**Synthesis of Poly(acroyl benzophene) macromonomer (Nb-PABP).** The monomer acroylbenzophene (ABP) was prepared by the coupling of 4-hydroxybenzophenone (HBP) with acryloyl chloride. HBP (2.5 g) and trimethylamine (2 mL) were dissolved in a round bottom flask with 20 mL acetone equipped with a stir bar. The flask was cooled to 0 °C. Acryloyl chloride (1.27 g) was dissolved in 5 mL acetone before adding dropwise to the reaction flask via an addition funnel. The reaction proceeded first for 3 hours at 0 °C followed by overnight at room temperature. Product was collected by filtration then extracted from 10 mL 1M HCl twice, 10 mL 1M Na2CO3 aqueous solution and 10 mL DI water. The product was dried with MgSO4, concentrated *in vacuo*, and white solid ABP was obtained (yield 1.87 g). RAFT polymerization of ABP monomer with Nb-CTA as the chain –transfer agent products Nb-PABP. NbCTA (17.5 mg, 0.031 mmol), ABP (443.8 mg, 1.76 mmol) and AIBN (0.54 mg, 0.003 mmol) were added to a 50 mL round bottom flask equipped with a stir bar and dissolved in 3.8 mL 1,4-dioxane. After purging with nitrogen gas for 30 minutes, the reaction proceeded at 65 °C for 25.5 hours. NbPABP was collected by precipitation in methanol three times. Yield: 11.5 mg; Mₙ 2265 g/mol, PDI 1.28 by GPC.

**Synthesis of Poly(N-isopropyl acrylamide) macromonomer (Nb-PNIPAAm).** NIPAAM (2.064 g, 18.24 mmol), NB-CTA (94.97 mg, 0.166 mmol), AIBN (2.71 mg, 1.66 ×10-2 mmol) and anhydrous 1,4-dioxane (20 mL) were mixed in a 100 mL RBF, and the solution was purged by bubbling with nitrogen for 30 minutes. The flask was sealed and polymerization was initiated by raising the temperature to 65 °C. Aliquots were withdrawn periodically for analysis by GPC, and when the desired molecular weight was obtained the flask was removed from heat, quenched in an ice bath, and the
polymer was recovered by several precipitations in diethyl ether to remove unreacted monomer.

**Synthesis of PNIPAAm-co-PABP Bottlebrush polymer (PNb(NIPAAm-c-ABP)).** All reactions were carried out in an oxygen and water-free glove box. The following is a representative synthesis of PNb(NIPAAm-c-ABP). NbPNIPAAm8k (100 mg, 0.0125 mmol) and NbPABP (0.87 mg, 0.0039 mmol) were added to a glass vial, equipped with a stir bar. Anhydrous, degassed DCM was added to the vial for a final solution concentration of 0.025 M (0.65 mL). A stock solution of Grubb’s second generation catalyst solution was prepared in a separate vial (2.0 mg, 0.002 mmol) in 1.5 mL DCM). For a target backbone DP of 50, 0.0043 mmol of catalyst (100 μL) was added to the stirring macromonomer flask and allowed to react for 2 hours at room temperature. To quench the reaction, the vial was removed from the glove box and approximately 100 μL of butyl vinyl ether was added. Bottlebrush was isolated by precipitation in cold ethyl ether and dried *in vacuo*. The product is a light yellow powder.

**Preparation of stable PNIPAAm-co-PABP bottlebrush films.** Si substrates were sonicated for 20 minutes each in 2 wt% soap solution, DI water, and IPA and dried with air. Freshly cleaned substrates were then placed in a piranha solution (3:1 concentrated H$_2$SO$_4$: 30% H$_2$O$_2$) at 80 °C for one hours. Films were then rinsed thoroughly with DI water to introduce hydrophilic surface with hydroxyl end-groups. The base layer is a poly(glycidyl methacrylate) (PGMA) formed from solution spin casting a 0.05 wt% PGMA in THF at 1500 rpm for 30 seconds. The PGMA layer is treated by thermally annealing at 110 °C for 20 minutes under vacuum to form a chemical bond between Si substrate and PGMA. Next the bottlebrush PNb(NIPAAm-c-ABP) was dissolved in dichloromethane at 2 wt % and spun cast directly onto the PGMA layer at 1500 rpm for 30 seconds. These two-layer films were annealed at 250 °C overnight then exposed to UV light at 360 nm to obtain stable films.

6.3.3 Results

6.3.3.1 Synthesis of crosslinkable NIPAAM bottlebrushes

Thermo-responsive bottlebrush polymers were synthesized by RAFT then ROMP “grafting-through” polymerization. PNIPAAm and PABP macromonomers were
synthesized separately by RAFT polymerization. Copolymerization of crosslinkable NbPABP and NbPNIPAAm linear side-chains results in a mixed-arm bottlebrush. PNIPAAm bottlebrushes are water-soluble only after an aminolysis reaction to remove the terminal CTA. A diagram of the synthetic strategy for PNb(NIPAAm-c-ABP) bottlebrushes is shown in Figure 6.4.

![Synthetic route diagram]

**Figure 6.4** Synthetic route to prepare water-soluble, crosslinkable PNb(NIPAAm-c-ABP) bottlebrush polymers.

6.3.3.2 Anti-Biofouling studies

Temperature dependent cell culture studies will be performed on crosslinked PNb(NIPAAm-c-ABP) bottlebrush to determine resistibility to bioadhesion. Crosslinked PNb(NIPAAm-c-ABP) films will first be compared to PNIPAAm films from linear
polymer and hydrophobic polystyrene films. We expect to observe decreased bioadhesion to PNb(NIPAAm-c-ABP) films as compared with the other two. Next, cell culture will be carried out at higher temperatures (T > T_{LCST}) such that the NIPAAM brushes are collapsed and insoluble in water creating a hydrophobic surface. The hydrophobic bottlebrush surface should increase cell adhesion. Then the cell attached films will be cooled below T_{LCST} and the cell attachment will be quantified. If the bottlebrush film swells with water as expected we should observe a decreased number of attached cells. PNIPAAm’s reversible solubility in water with temperature make it an ideal candidate for anti-biofouling studies.

6.3.3.3 Fluorescent NIPAAM bottlebrushes

Fluorescent water soluble bottlebrush polymers were synthesized by RAFT copolymerization of NIPAAm monomer with fluorescence methacrylate (FMA), a fluorescent molecule. RAFT was carried out at 65 °C for 2 hours with NbCTA:AIBN:NIPAAm:FMA in a 1:0.1:60:0.52 ratio yielding PNIPAAm-co-PFMA macromonomer, NbP(NIPAAm-c-FMA). ROMP polymerization of the terminal norbornene group yielded bottlebrush polymer with NIPAAm-c-FMA side-chains, PNBp(NIPAAm-c-FMA). The chemical structures of the macromonomer and bottlebrush polymer are shown in Figure 6.5. The fluorescent properties of NbP(NIPAAm-c-FMA) bottlebrush polymers are demonstrated in Figure 6.6.
**Figure 6.5** Chemical structure of fluorescent, water soluble NbP(NIPAAm-c-FMA) macromonomer and PNbP(NIPAAm-c-FMA)_n bottlebrush polymers after ROMP.

**Figure 6.6** Fluorescent bottlebrush polymer dry (left vial) and in water (right vial) in white and UV light.
6.4 Conclusion

We have discussed future applications of bottlebrush polymer research for use as additives to modify thermal properties of polymer nanocomposites and as anti-biofouling coatings. Bottlebrush polymers as additives in polymer nanocomposites may be an attractive system from a theoretical perspective, however in practice trends in $T_g$ for blends of bottlebrush polymers with linear polymers have been difficult to achieve. Furthermore bottlebrush/linear blends do not result in large changes in thermal properties reported in solid nanoparticle additives (such as graphene or silica nanoparticles), which is expected but may not be useful from an industrial prospective. In my opinion, a more promising future direction for bottlebrush polymers is as additives in thin films.

Bottlebrush polymers for additives in polymer films present a great potential application for these specialized materials. In Chapter 4 of this thesis we demonstrated that bottlebrush polymers can spontaneously segregate to the polymer-air interface and impart significant changes to the surface properties, such as surface hydrophobicity. While this phenomenon needs to be studied further to determine if high surface-energy bottlebrush polymers will also spontaneously segregate to the top surface, it represents a significant advantage of bottlebrush polymers over conventional linear copolymers. For anti-fouling applications, bottlebrush polymers with thermoresponsive properties could be blended with bulk linear polymers and solution casted on coat large surfaces. Bottlebrushes can segregate to the polymer-air interface which provides a brush layer on the exposed film surface that will instill anti-biofouling properties to the surface with minimal additives. Additionally the thermoresponsive nature of NIPAAm side-chains could allow a self-cleaning procedure by simply heating the surface above a certain temperature ($T_{LCST} \sim 37 \, ^\circ C$). Bottlebrush polymers are more expensive to make and process than conventional linear polymers, therefore an application that utilizes minimal bottlebrushes as additives would be much more appealing than using bottlebrush polymers in bulk.
6.5 References


(10) Oh, H. G., Peter F. Nat Mater 2009/02//print, 8, 139.


6.6 Supplemental Information

6.6.1 Matlab code

function Phase_Diagram_Generation
clc; clear all;
% Phase figure
poly = input('Polymer type (use single quotes) = ');
n = 1;
% following loop can indicate different fillers, but not used because only
% one filler considered at a time
for l= 1:n
    fill{l} = input('Filler types (use single quotes) = ');
end
% filler contact angle
% enter first angle as the last angle as well (4 entries in all) for the
% function to properly average everything
% order of the matrices: [forma diiodo water forma]
% includes filler properties and the contact angle

CA = [60.2 56.3 79.4 60.2]; %updated with PLABBP Ashley data 6-23-2015
% solvent properties
% dispersive
fillld = [39 50.8 21.8 39];
% polar
filllp = [19 0 51 19];
% automated surface energy solver
for i = 1:length(fillld)-1
    yld1 = fillld(i); ylp1 = filllp(i); yld2 = fillld(i+1); ylp2 = filllp(i+1);
    cost1 = cos(CA(i)/180*pi); cost2 = cos(CA(i+1)/180*pi);
    yl1 = yld1 + ylp1; yl2 = yld2 + ylp2;
    a1 = (yl1*(1+cost1)/2)/sqrt(yld1);
    a2 = (yl2*(1+cost2)/2)/sqrt(yld2);
    b2 = sqrt(ylp2/yld2); b1 = sqrt(ylp1/yld1);
    syms ysp
    ysp1(i) = (a2-a1)^2/((b2-b1)^2);
    ysd(i) = (1/yl1)*((y1*(1+cost1)/2)-sqrt(ylp1*ysp1(i)))^2;
end
% filler surface energies - un-semicolon these staments
%polar surface energy
fillyfp = sum(ysp1)/length(ysp1);
%dispersive surface energy
fillyfd = sum(ysd)/length(ysd);
fillyf = fillyfp+fillyfd;
% For the polymer surface energy calculations, similar set up as the filler

CAp = [78.4 32.3 89.0 78.4]; %PS films Ashley data 6-23-2015
ld = [39 50.8 21.8 39];
lp = [19 0 51 19];
for i = 1:length(ld)-1
    yld1 = ld(i); ylp1 = lp(i); yld2 = ld(i+1); ylp2 = lp(i+1);
    cost1 = cos(CAp(i)/180*pi); cost2 = cos(CAp(i+1)/180*pi);
```
y11 = yld1 + ylp1; yl2 = yld2 + ylp2;
a1 = (y11*(1+cost1)/2)/sqrt(yld1);
a2 = (y12*(1+cost2)/2)/sqrt(yld2);
b2 = sqrt(ylp2/yld2); b1 = sqrt(ylp1/yld1);
syms ysp
ysp1(i) = (a2-a1)^2/((b2-b1)^2);
ysd(i) = (1/yld1)*((y11*(1+cost1)/2)-sqrt(ylp1*ysp1(i)))^2;
end

% polymer surface energies - un-semicolon these statements
% polar surface energy
ypp = sum(ysp1)/length(ysp1)
% disperisve surface energy
ypd = sum(ysd)/length(ysd)

% construct phase lines for iso angle
ang = [0,pi/6,pi/4];
% ang = input('Enter iso angle constraints: ')
[iay,iax] = isoangle(ang,ypp,ypd);
ang = ang*180/pi;
% iso contact angle plot
for i = 1:length(ang)
    plot(iax(:,i),iay(:,i),'b')
    str = [num2str(ang(i)),char(176)];
    s1 = double(iax(100,i));
    s2 = double(iay(100,i));
    t(i) = text(s1,s2,str);
    set(t(:,),'fontw','bold','fonts',12)
    hold on
end
s3 = double(iax(160,i));
s4 = double(iay(160,i));
text(s3,s4,'Iso Contact Angle Lines')
% construct phase lines for iso work of spreading
Ws = [-10,-5,0,5,10];
% Ws = input('Enter iso work of spreading constraints: ')
[wsy,wsx] = isospreading(Ws,ypp,ypd);
% iso work of spreading plot
for j = 1:length(Ws)
    plot(wsx(:,j),wsy(:,j),'r')
    str = [num2str(Ws(j))];
    s1 = double(wsx(90,j));
    s2 = double(wsy(90,j));
    t(j+i) = text(s1,s2,str);
    set(t(:,),'fontw','bold','fonts',12)
    hold on
end
s3 = double(wsx(40,j));
s4 = double(wsy(40,j));
text(s3,s4,'Iso Work of Spreading Lines')
% construct phase lines for iso relative work
Wa = [.2,2,5,10];
% Wa = input('Enter iso relative work constraints: ')
[way,wax] = isorelative(Wa,ypp,ypd);
for k = 1:length(Wa)
    plot(wax(:,k),way(:,k),'k')
end
```

str = [num2str(Wa(k))];
s1 = double(wax(28,k));
s2 = double(way(28,k));
t(k+j+i) = text(s1,s2,str);
set(t(:,),'fontw','bold','fonts',12)
hold on
end
s3 = double(wax(50,k));
s4 = double(way(50,k));
text(s3,s4,'Iso Relative Work Lines')
text(25,5,poly);
plot(fillyfp,fillyf,'r*')
for m = 1:1:length(fill)
text(fillyfp(m),fillyf(m),fill{m});
end
ylabel('$\gamma_f$, $mJ/m^2$ Total Surface Energy','interpreter','latex','fontsize',12);
xlabel('$\gamma_f^p$, $mJ/m^2$ Polar Surface Energy','interpreter','latex','fontsize',12);
end
function [z,y] = isoangle(ang,ypp,ypd)
% loop for each angle specification
for i = 1:1:length(ang)
    % define bounds for yfp by finding max yfp
    syms yfpmax
    yfpm = solve(((1+cos(ang(i)))*(ypp*yfpmax)^(1/2)+ypd)^2-
    (1+cos(ang(i)))^2*yfpmax*(ypp+ypd));
    yfpm = single(yfpm);
    yfp = linspace(0,yfpm(1),100);
    % solve for total surface energy
    a = (1+cos(ang(i)))^2/4;
    b = -(1+cos(ang(i)))*(ypp.*yfp).^(1/2)-ypd;
    c = yfp.*(ypp+ypd);
    r1 = (-b+(b.^2-4*a.*c).^(1/2))/(2*a);
    r2 = (-b-(b.^2-4*a.*c).^(1/2))/(2*a);
    % coalesce data
    y(:,i) = [yfp,fliplr(yfp)];
    z(:,i) = [r1,fliplr(r2)];
end
end
function [z,y] = isospreading(Ws,ypp,ypd)
% loop for each angle specification
for i = 1:1:length(Ws)
    yfp = linspace(0,40,100);
    C = (Ws(i)/2)+ypd+ypp;
    yf = (1/ypd)*(ypd.*yfp-(2*C.*(ypp.*yfp).^(1/2))+(ypp.*yfp)+C^2);
    r1 = yf;
    % coalesce data
    y(:,i) = yfp;
    z(:,i) = r1;
end
end
function [z,y] = isorelative(Wa,ypp,ypd)
% loop for each angle specification
for i = 1:1:length(Wa)
    % define bounds for yfp by finding max yfp
    syms yfpmm
    yfpb = solve(-2*ypp+4*(ypp*yfpmm)^(1/2)+Wa(i)-2*yfpmm);
    yfpb = double(yfpb);
    if length(yfpb) == 1
        yfpb(2) = yfpb(1);
        yfpb(1) = 0;
    end
    yfp = linspace(yfpb(1),yfpb(2),100);
    % solve for total surface energy
    a = -2*ypd*ypp+4*ypd*(ypp)^(1/2).*((ypp)^(1/2)).*(yfp)^(1/2)+ypd*Wa(i)-
    2*ypd.*yfp;
    b = 2*ypd-2*ypp+4*(ypp^(1/2)).*(yfp.(1/2))+Wa(i);
    r1 = 0.5*((2*sqrt(2).*(a.^((1/2))))+b);
    r2 = 0.5*(-(2*sqrt(2).*a.^((1/2)))+b);
    % coalesce data
    y(:,i) = [yfp,fliplr(yfp)];
    z(:,i) = [r1,fliplr(r2)]';
end
end