Synthesis and Self-Assembly of Bottlebrush Block Polymers: Molecular Architecture and Materials Design

Thesis by

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Garret was my mentor when I first joined the group as a summer (SURF) student, and he introduced me to polymer chemistry and the potential of polymer-based materials. We wrote a review together after I joined the group as a grad student, and I included an overview of the challenges in the field. Garret returned that section unmarked — all discussion of present limitations intact — except he crossed out *challenges* and replaced *opportunities*. I rolled my eyes! However, Garret's edit and enthusiasm echo now when I think about new research directions.

I started to work with Chris during my first year as a grad student, shortly after Chris joined the group as a postdoc. Chris introduced me to polymer physics, and we worked together on several aspects of this thesis, including the phase behavior of low-χ block polymers (Chapter 4) and brush polymer electrolytes (Chapter 6-2). Working with Chris taught me many valuable skills, including how to finish a project and how to write a paper, as well as the value of building diverse interests. At any point, Chris may be reading a textbook on X-ray diffraction or statistical thermodynamics or organic reaction mechanisms, and his creativity in connecting different ideas was inspiring.

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We have been tremendously fortunate to collaborate with members of the scientific community outside Caltech. Their contributions have crucially enabled the work presented in this thesis. I would like to express my deep appreciation for their expertise and insight, as well as my sincere hope that we will continue to find opportunities to collaborate. I will thank our collaborators in the approximate order of the first appearance of their contributions in this thesis.

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I would also like to thank our collaborators at the University of Minnesota: **Ingrid Haugan, Dr. Michael Maher**, **Prof. Marc Hillmyer**, and **Prof. Frank Bates**. They performed the studies described in Chapter 3-3 to explore the effects of grafting density on linear rheological properties. I greatly appreciate the opportunity to learn more about rheology and these materials through their efforts. I would additionally like to thank Frank for his valuable suggestions regarding partial mixing in our low-χ brush block polymers (Chapter 4), as well as **Drs. Sid Chanpuriya**, **Matt Irwin**, and **Tuoqi Li** for their assistance with microtomy.

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Prof. Mark Matsen at the University of Waterloo played a key role in our work studying the effects of low-χ block polymer design (Chapter 4). His SCFT calculations helped guide our molecular interpretation of the unusual phase behavior. In this and several other contexts, Mark was immediately ready with a compelling explanation — and not only an explanation, but a relevant reference from his previous work! I appreciate his insight and, through our work together, the opportunity to see how simulations can help build physical models.

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ABSTRACT

Bottlebrush polymers represent a unique molecular architecture and a modular platform for materials design. However, the properties and self-assembly of bottlebrush polymers remain relatively unexplored, in large part due to the synthetic challenges imposed by the sterically demanding architecture. This thesis describes our work to close this gap, connecting (1) the synthesis of polymers with precisely tailored molecular architectures, (2) the study of fundamental structure-property relationships, and (3) the design of functional materials.

Chapter 1 introduces key concepts related to polymer architecture and block polymer phase behavior. Recent developments in the synthesis and self-assembly of bottlebrush block polymers are highlighted in order to frame the work presented in Chapters 2–6.

Chapter 2 introduces a versatile strategy to design polymer architectures with arbitrary side chain chemistry and connectivity. Simultaneous control over the molecular weight, grafting density, and graft distribution can be achieved via living ring-opening metathesis polymerization (ROMP). Copolymerizing a macromonomer and a small-molecule co-monomer provides access to well-defined polymers spanning the linear, comb, and bottlebrush regimes. This design strategy creates new opportunities for molecular and materials design.

Chapter 3 explores the physical consequences of varying the grafting density and graft distribution in two contexts: block polymer self-assembly and linear rheological properties. The molecular architecture strongly influences packing demands and therefore the conformations of the backbone and side chains. Collectively, these studies represent progress toward a universal model connecting the chemistry and conformations of graft polymers.

Chapter 4 discusses the phase behavior of ABA' and ABC bottlebrush triblock terpolymers. Low-χ interactions between the end blocks promote organization into a unique mixed-domain lamellar morphology, LAM$_{\mathrm{P}}$. X-ray scattering experiments reveal an unusual trend: the domain spacing strongly *decreases* with increasing total molecular weight. Insights

into this behavior provide new opportunities for block polymer design with potential consequences spanning all self-assembling soft materials.

Chapter 5 describes other physical consequences of low-χ block polymer design. The ternary phase diagrams for ABC, ACB, and BAC bottlebrush triblock terpolymers reveal the influences of low-χ A/C interactions, frustration, and the molecular architecture. Potential non-equilibrium effects and crystallization in these bottlebrush polymers will also be discussed.

Chapter 6 describes applications of bottlebrush polymers as functional materials. Self-assembly enables mesoscale structural control over many materials properties, such as reflectivity, conductivity, and modulus. The synthetic methods (Chapter 2) and physical insights (Chapters 3−5) provided in previous chapters illustrate opportunities for materials design. We will discuss AB brush diblock polymers that self-assemble to photonic crystals and ABA brush triblock copolymers in solid polymer electrolytes.

PUBLISHED CONTENT AND CONTRIBUTIONS

The work in this thesis includes content from the following published or submitted manuscripts. This work was enabled by the contributions of all authors, which are described in the acknowledgments and reflected throughout the thesis. In the interest of brevity, only contributions by A.B.C. have been identified below, except where appropriate to acknowledge other authors in the same role.

Chapter 2: Control over the Graft Polymer Architecture via Ring-Opening Metathesis Polymerization

1. Lin, T.-P.; Chang, A. B.; Chen, H.-Y.; Liberman-Martin, A. L.; Bates, C. M.; Voegtle, M. J.; Bauer, C. A.; Grubbs, R. H. Control of Grafting Density and Distribution in Graft Polymers by Living Ring-Opening Metathesis Copolymerization. *J. Am. Chem. Soc.* **2017**, *139*, 3896–3903. doi: 10.1021/jacs.7b00791.

   A.B.C. designed the study (with T.-P.L. and C.M.B.), performed some of the macromonomer synthesis and homo- and copolymerization experiments, interpreted data, and contributed to manuscript preparation.

2. Chang, A. B.;$^+$ Lin, T.-P.;$^+$ Thompson, N. B.; Luo, S.-X.; Liberman-Martin, A. L.; Chen, H.-Y.; Grubbs, R. H. Design, Synthesis, and Self-Assembly of Polymers with Tailored Graft Distributions. *J. Am. Chem. Soc.* **2017**, *139*, 17683–17693. doi: 10.1021/jacs.7b10525. ($^+$*Equal contributions.*)

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Chapter 3: Impacts of the Graft Polymer Architecture on Physical Properties

3. Lin, T.-P.;$^+$ Chang, A. B.;$^+$ Luo, S.-X.; Chen, H.-Y.; Lee, B.; Grubbs, R. H. Effects of Grafting Density on Block Polymer Self-Assembly: From Linear to Bottlebrush. *ACS Nano* **2017**, *11*, 11632–11641. doi: 10.1021/acsnano.7b06664. ($^+$*Equal contributions.*)

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Chapter 4: Manipulating the ABCs of Self-Assembly via Low-χ Block Polymer Design

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6. Sunday, D. F.;* Chang, A. B.;* Liman, C. D.; Gann, E.; DeLongchamp, D. M.; Matsen, M. W.; Grubbs, R. H.; Soles, C. L. Evidence for Backbone Flexibility of Bottlebrush Block Copolymers Driven by Low-χ Assembly. **2018**. *submitted.* (**Corresponding authors.*)

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Chapter 6: Applications of Bottlebrush Polymers in Functional Materials

7. Macfarlane, R. J.; Kim, B.; Lee, B.; Weitekamp, R. A.; Bates, C. M.; Lee, S. F.; Chang, A. B.; Delaney, K. T.; Fredrickson, G. H.; Atwater, H. A.; Grubbs, R. H. Improving Brush Polymer Infrared One-Dimensional Photonic Crystals via Linear Polymer Additives. *J. Am. Chem. Soc.* **2014**, *136*, 17374–17377. doi: 10.1021/ja5093562.

   A.B.C. imaged all samples by scanning electron microscopy and provided edits to the manuscript.

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9. Bates, C. M.; Chang, A. B.; Schulze, M. W.; Momčilović, N.; Jones, S. C.; Grubbs, R. H. Brush Polymer Ion Gels. *J. Polym. Sci., Part B* **2016**, *54*, 292–300. doi: 10.1002/polb.23927.

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    A.B.C. synthesized the polymers, collected and analyzed X-ray scattering data, and provided edits to the manuscript.

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