

Tailoring Surface Properties of Polymer Films with Bottlebrush Copolymers

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Nilesh Charpota

December 2024

© by Nilesb Charpota, 2024
All Rights Reserved.

For my parents and sisters, without whom I have never gotten this far.

Acknowledgements

I would like to thank my advisor Dr. Gila Stein for her continuous support during the period of my doctorate. It would be an understatement to say she has been the best mentor during my time at the University of Tennessee. I have had an incredible opportunity to learn from such an amazing mentor and scientist. I would also like to thank all my lab members Dr. Jonathan Coote and Dr. Karthika Madathil for guiding me while starting and giving me some great recommendations that I have implemented and remembered for quite a while. I would also like to thank Dr. Travis Laws who has played a significant role in mentoring me during the initial phase of my doctorate. I want to thank our collaborators from Rice University, in particular, Dr. Rafael Verduzco and Dr. Dongjoo Lee, especially, for their role in our work on the "Impact of processing effects on surface segregation of bottlebrush polymer additives". I have thoroughly enjoyed working with and sharing ideas during our collaboration. I would also like to express my appreciation to Laura Brady, whose efforts have allowed me to work on the final part of my dissertation, along with all the other graduate students in the chemical engineering department and collaborators both in our lab and outside with whom I have enjoyed working and bonded over the years.

Finally, I'd like to thank my family, their unwavering support and encouragement throughout this entire journey have pushed me to become a better person and a scientist.

“Many people are passionate, but because of their limiting beliefs about who they are and what they can do, they never take actions that could make their dream a reality.”

- by Tony Robbins

Abstract

Bottlebrush polymers are a class of branched polymers with polymeric side chains densely grafted to a linear backbone. Due to their tunable chemistry and architecture, bottlebrush polymers can be used as surface-active additives that tailor surface properties, or as thin film coatings that mimic the functions of surface-attached polymer brushes. My research has encompassed the design, synthesis, and characterization of bottlebrush copolymers having a mixture of polystyrene (PS) and poly(2-vinylpyridine) (P2VP) side chains. PS is hydrophobic with a low surface energy, while P2VP is hydrophilic with a high surface energy. This dissertation consists of two original research thrusts. The first thrust focuses on designing wetting reversal processes, wherein bottlebrush PS-co-P2VP accumulates at the surface of PS films despite an approximately 15% gain in surface energy. The wetting reversal is mediated by a strong entropic attraction of the bottlebrush copolymer towards surfaces. These studies establish the conditions where wetting reversals are thermodynamically stable, and it is anticipated that this knowledge could be extended to chemistries beyond PS and P2VP. The second research thrust focuses on the structure and surface properties of bottlebrush PS-co-P2VP, where the fraction of P2VP side chains and the molar composition of 2-vinylpyridine are independently varied. These materials have a mixture of PS and P2VP side chains at the surface when bottlebrush PS-co-P2VP is weakly segregated, while a PS wetting layer forms at the surface when bottlebrush PS-co-P2VP is more strongly segregated and able to self assemble into nanoscale

domains. In the limit of weak segregation, wettability and surface energy scale with the fraction of P2VP side chains.

Table of Contents

1	Introduction	1
2	Synthesis	6
2.1	RAFT polymerization	6
2.2	Ring Opening Metathesis Polymerization (ROMP)	11
2.2.1	Bottlebrush Polymers	14
2.2.2	Research methodology and alternate approach for synthesizing bottlebrush polymers	16
2.2.3	Significance of the Anchor Group in Ring-Opening Metathesis Polymerization	18
3	Methods	23
3.1	Surface Energy Measurement	23
3.1.1	Contact Angle Measurement	27
3.1.2	Models for solid-liquid interfacial energy measurement	30
3.2	Time-of-flight secondary ion mass spectrometry (ToF-SIMS)	32
3.2.1	Introduction	32
3.2.2	Depth profiling of polymer blends	34
3.2.3	Processing ToF-SIMS raw data	35
4	Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers	40

4.1	Introduction	40
4.2	Experimental	43
4.2.1	Synthesis of Bottlebrush and Linear Polymers	43
4.2.2	Characterization	48
4.3	Results	50
4.4	Discussion	63
4.5	Conclusions	65
5	Surface Properties of Thin Films of Bottlebrush Statistical Copolymers	67
5.1	Introduction	67
5.2	Experimental	68
5.2.1	Materials	68
5.2.2	ROMP Kinetics.	70
5.2.3	Characterization	72
5.3	Results and Discussion	74
5.4	Conclusions	85
6	Outlook	87
	Bibliography	90
A	Supporting Characterization for: Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers.	101
A.1	^1H NMR	101
A.2	Gel Permeation Chromatography (GPC)	112
A.3	Contact Angle Measurements	114
A.4	Microscopy and TOF-SIMS	117
A.5	Linear P2VP/Linear PS Blends	121

B Supplemental Characterization for: Surface Properties of Thin Films of Bottlebrush Statistical Copolymers.	125
B.1 ^1H NMR	125
B.2 Gel Permeation Chromatography (GPC)	143
B.3 Contact Angle Measurements	147
B.4 ^1H NMR for kinetic studies.	148
C Calculations	171
Products	174
Vita	175

List of Tables

4.1	Characteristics of PS macromonomer, linear PS, and linear P2VP. M_n is the number-average molecular weight, N_i is the degree of polymerization, $\bar{D}$ is the dispersity.	54
4.2	Characteristics of bottlebrush copolymers. M_w is the weight-average molecular weight; N_b is the average backbone degree of polymerization; $\bar{D}$ is the backbone dispersity; N_{P2VP}^{GPC} is the average degree of polymerization of free P2VP homopolymer from GPC; $\bar{D}_{P2VP}$ is the dispersity of free P2VP homopolymer from GPC; f is either the mol% of NB-CTA in precursor bottlebrush (B_1 - B_4) or mol% of 2-vinylpyridine in the final bottlebrush copolymer (BB_1 - BB_4); N_{P2VP}^{NMR} is the average degree of polymerization of P2VP side chains from NMR.	54
4.3	Characteristics of each blend. N_m/N_{PS} is the chain length ratio of PS host to PS side chains, and N_{P2VP}/N_{PS} is the chain length ratio of P2VP and PS side chains.	56
5.1	Characteristics of NB-PS macromonomers and linear random copolymers of (S) and (2VP). M_n is the number-average molecular weight, N_i is the degree of polymerization, $\bar{D}$ is the dispersity, and f is the mol% of 2-vinylpyridine in the copolymer.	75

5.2	Characteristics of bottlebrush copolymers. M_w is the weight-average molecular weight; N_b is the average backbone degree of polymerization; $\bar{D}$ is the backbone dispersity; N_{P2VP}^{GPC} is the average degree of polymerization of free P2VP homopolymer from GPC; $\bar{D}_{P2VP}$ is the dispersity of free P2VP homopolymer from GPC; f is either the mol fraction of NB-CTA in precursor bottlebrush (B_1 - B_{10}) or mol fraction of 2-vinylpyridine in the final bottlebrush copolymer (BB_1 - BB_{10}); N_{P2VP}^{NMR} is the average degree of polymerization of P2VP side chains from NMR.	76
A.1	List of test fluids used for surface energy calculations for pure PS, pure P2VP, as-cast films for all blends and annealed films for all blends, (X) indicates test fluid used for surface energy measurements and (-) indicates test fluids not used for surface energy measurements.	115

List of Figures

2.1	Mechanism of RAFT polymerization. Image reproduced from reference [30].	8
2.2	Typical RAFT agent with required properties of (R) and (Z) group. Image reproduced from reference [31].	10
2.3	General mechanism of a ring-opening metathesis polymerization (ROMP). Image reproduced from reference [37].	13
2.4	A simple schematic of bottlebrush polymer where N_{sc} is side chain degree of polymerization and N_b is backbone degree of polymerization.	15
2.5	Representation of a grafting-to, grafting-through and grafting-from reaction to synthesize bottlebrush polymers. Image reproduced from reference [42].	17
2.6	Scheme for the synthesis of P2VP/PS bottlebrush copolymers via a combination of "grafting through" and "grafting from" methods. . . .	19
2.7	Structures for three macromonomers (MMs) used by Radzinski and coworkers with three different anchor groups. Depicting possible chelation between the Ru metal center and carbonyl oxygen present in the anchor group along with regio-isomers unlikely to form chelates. Image reproduced from reference [45].	21

2.8	(a). Results for kinetic analysis for ROMP of polystyrene MMs (Mw = 3 kDa) where [MM]/[G3] ratio = 100 and concentration 50 mg/ml (green circle = 1S _{3k} , blue circle = 2S _{3k} and red circles = 3S _{3k}) (b). SEC traces for the kinetic study for PS MM (t = 1, 2, 5, 10 and 30 min) for 1S _{3k} . Image reproduced from reference [45].	22
3.1	Imbalance in inter-molecular forces between molecules at the bulk or surface. Image reproduced from reference [52].	24
3.2	Equilibrium of forces during a liquid wetting a solid according to Young's equation. Image reproduced from reference [54].	26
3.3	A brief overview of contact angle measurement process using a contact angle goniometer. Image reproduced from reference [56].	28
3.4	Image of a liquid's droplet with clear visible edges.	29
3.5	Overview of a ToF-SIMS instrument. Image reproduced from reference [65].	33
3.6	Si ⁺ signal versus scan number plot for P2VP/PS bottlebrush blend with linear PS.	36
3.7	C ₇ H ₈ N ⁺ / C ₇ H ₇ ⁺ signal ratio versus depth plot for P2VP/PS bottlebrush blend with linear PS.	38
3.8	C ₇ H ₈ N ⁺ / C ₇ H ₇ ⁺ signal ratio versus depth (%) plot for P2VP/PS bottlebrush blend with linear PS.	39
4.1	(Left) Depiction of bottlebrush PS- <i>co</i> -P2VP and linear PS architectures. (Right) Synthesis of bottlebrush PS- <i>co</i> -P2VP by a hybrid "grafting-through" and "grafting-from" approach. The molecular fragments colored red and blue are detected in time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of blends.	52

4.2	Surface energies (γ_s) for as-cast (AC) and thermally annealed (ANN) films of (a) bottlebrush copolymer; (b) blends S11 (BB ₁ /PS ₂), S15 (BB ₁ /PS ₃) and S1 (BB ₁ /PS ₁); (c) blends S15 (BB ₁ /PS ₃), S16 (BB ₂ /PS ₃), S17 (BB ₃ /PS ₃) and S18 (BB ₄ /PS ₃); (d) blends S1 (BB ₁ /PS ₁), S3 (BB ₂ /PS ₁), S5 (BB ₃ /PS ₁), and S7 (BB ₄ /PS ₁). Dispersive (γ_s^d) and polar (γ_s^p) components are represented by red and blue, respectively. Surface energies of P2VP and PS homopolymer are included as references.	56
4.3	TOF-SIMS depth profiles. Top Row: Blends S11 (BB ₁ /PS ₂), S15 (BB ₁ /PS ₃), and S1 (BB ₁ /PS ₁), both as-cast (a) and annealed (b). Middle row: Blends S15 (BB ₁ /PS ₃), S16 (BB ₂ /PS ₃), S17 (BB ₃ /PS ₃), and S18 (BB ₄ /PS ₃), both as-cast (c) and annealed (d). Bottom row: Blends S1 (BB ₁ /PS ₁), S3 (BB ₂ /PS ₁), S5 (BB ₃ /PS ₁), and S7 (BB ₄ /PS ₁), both as-cast (e) and annealed (f).	58
4.4	From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S15 (BB ₁ /PS ₃) (a) as-cast and (b) annealed at 140 °C for 48 hrs.	62
4.5	From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S7 (BB ₄ /PS ₁) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	62

5.1	ROMP kinetics for (a) NB-PS39 homopolymerization with G3; (b) NB-CTA homopolymerization with G3; (c) copolymerization of NB-PS39 and NB-CTA at a molar ratio of 40:60 with G3; (d) NB-PS39 homopolymerization with G1/PPh3; (e) NB-CTA homopolymerization with G1/PPh3; and (f) copolymerization of NB-PS39 and NB-CTA at a molar ratio of 50:50 with G1/PPh3. Solid lines in parts a, d, and e report the best fit to $\rho = 1 - e^{-k_{pt}t}$. Dashed lines in parts b, c and f are a guide to the eye. All tests used a monomer-to-catalyst molar ratio of 100:1.	80
5.2	SAXS data for annealed films of bottlebrush PS-co-P2VP, grouped by the percentage of side chains that are P2VP. (a) 60% P2VP side chains; (b) 30% P2VP side chains; (c) 50% P2VP side chains. The Kapton substrate is included as a reference.	83
5.3	Plots for total surface energy vs mole percent of 2-vinylpyridine (a) as-cast (b) annealed at 140 °C for 48 hrs. And plots for total surface energy vs number of repeat units of 2-vinylpyridine (c) as-cast and (d) annealed at 140 °C for 48 hrs.	86
A.1	NMR spectrum for exo-5-norbornene-2-carboxylic acid.	102
A.2	NMR spectrum for norbornene methanol (NB-MeOH).	102
A.3	NMR spectrum for NB-CTA. The appearance of the CTA peak (b, 2H, 3.25 ppm) confirms a successful coupling reaction.	103
A.4	NMR spectrum for NB-PS. The protons from styrene (a, 5H, 6.25-7.3 ppm) were integrated relative to the protons from norbornene (b, 2H, 6.1 ppm) to obtain the average degree of polymerization of the polymer.	103

A.5	NMR spectrum for B ₁ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm) and (c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. The styrene peak contains PS from precursor bottlebrush and unincorporated PS. The relative amounts were determined from GPC.	104
A.6	NMR spectrum for BB ₁ and linear P2VP. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 ppm; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain the mole percent of each polymer.	104
A.7	NMR spectrum for BB ₁ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	105
A.8	NMR spectrum for B ₂ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.	106
A.9	NMR spectrum for B ₃ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.	107

A.10 NMR spectrum for B ₄ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.	108
A.11 NMR spectrum for BB ₂ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB ₂ structure.	109
A.12 NMR spectrum for BB ₃ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB ₃ structure.	110
A.13 NMR spectrum for BB ₄ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB ₄ structure.	111
A.14 GPC traces for BB-(PS- <i>co</i> -CTA) for (a) B ₁ (72% B ₁ and 28% unincorporated PS), (b) B ₂ (80% B ₂ and 20% unincorporated PS), (c) B ₃ (75% B ₃ and 25% unincorporated PS), (d) B ₄ (80% B ₁ and 20% unincorporated PS). All materials have free (unincorporated) PS chains from PS that was not functionalized with NB.	112
A.15 Combined GPC traces for the mixture of BB-(PS- <i>co</i> -P2VP) with free linear P2VP chains and the final BB-(PS- <i>co</i> -P2VP) product. (a) BB ₁ ; (b) BB ₂ ; (c) BB ₃ ; (d) BB ₄	113

A.16 OWRK fit for contact angle of (a) PS ($\gamma_s = 41.87 \pm 0.19$, $\gamma_s^d = 41.43 \pm 0.18$, $\gamma_s^p = 0.43 \pm 0.02$) (b) P2VP ($\gamma_s = 53.15 \pm 0.70$, $\gamma_s^d = 50.36 \pm 0.67$, $\gamma_s^p = 2.77 \pm 0.21$) (c) Sample S3 as-cast ($\gamma_s = 48.20 \pm 0.83$, $\gamma_s^d = 48.03 \pm 0.83$, $\gamma_s^p = 0.16 \pm 0.04$) (d) Sample S3 annealed ($\gamma_s = 41.67 \pm 0.67$, $\gamma_s^d = 41.43 \pm 0.67$, $\gamma_s^p = 0.23 \pm 0.05$). Surface energy units = mN/m.	116
A.17 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S16 (BB ₂ /PS ₃) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	117
A.18 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S17 (BB ₃ /PS ₃) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	118
A.19 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image, for blend S18 (BB ₄ /PS ₃) (a) as-cast and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	118
A.20 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S1 (BB ₁ /PS ₁) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	119
A.21 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S3 (BB ₂ /PS ₁) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the Silicon substrate.	119

A.22 From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S5 (BB ₃ /PS ₁) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.	120
A.23 GPC trace for Linear P2VP.	121
A.24 NMR spectrum for low molecular weight linear P2VP.	122
A.25 TOF-SIMS depth profiles for thin films of Linear P2VP/Linear PS ₁ , both as-cast and annealed, for (a) 2 wt% P2VP and (b) 10 wt% P2VP. The ratio of C ₇ C ₈ N ⁺ to C ₇ H ₇ ⁺ signals is proportional to the concentration of P2VP. The polymer-air interface is at depth = 0 % and the polymer-substrate interface is at depth = 100 %.	122
A.26 Surface energies for thin film blends of Linear P2VP/Linear PS ₁ , as-cast and annealed at 140 °C for 48 hours. Blends with 2 wt% and 10 wt% loading of P2VP.	123
A.27 3D TOF-SIMS images for blends of Linear P2VP/Linear PS ₁ , 2 wt% P2VP, (a) as-cast and (b) annealed at 140 °C for 48 hours. 3D TOF-SIMS images for blends of Linear P2VP/Linear PS, 10 wt% P2VP, (c) as-cast and (d) annealed at 140 °C for 48 hours.	124
B.1 NMR spectrum for NB-PS39.	126
B.2 NMR spectrum for NB-PS96.	126
B.3 NMR spectrum for P2VP macromolecule. The protons from 2-vinylpyridine (a, 3H, 6.3-7.3 PPM; c, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n . . .	127
B.4 NMR spectrum for P(S-co-2VP) ₁ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer.	128

B.5	NMR spectrum for P(S-co-2VP) ₂ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer	129
B.6	NMR spectrum for P(S-co-2VP) ₃ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer	130
B.7	NMR spectrum for P(S-co-2VP) ₄ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer	131
B.8	NMR spectrum for B _{5,6,7} . The protons from styrene in bottlebrush (a, 5H, 6.25-7.3 ppm) and styrene from unreacted polystyrene (c, 5H, 6.25-7.3 ppm) were integrated relative to the proton from CTA (b, 2H, 3.25 ppm) to obtain mole percent of each polymer.	132
B.9	NMR spectrum for B _{8,9,10} . The protons from styrene in bottlebrush (a, 5H, 6.25-7.3 ppm) and styrene from unreacted polystyrene (c, 5H, 6.25-7.3 ppm) were integrated relative to the proton from CTA (b, 2H, 3.25 ppm) to obtain mole percent of each polymer.	133
B.10	NMR spectrum for BB ₅ + Linear P2VP.	134
B.11	NMR spectrum for BB ₆ + Linear P2VP.	134
B.12	NMR spectrum for BB ₇ + Linear P2VP.	135
B.13	NMR spectrum for BB ₈ + Linear P2VP.	135
B.14	NMR spectrum for BB ₉ + Linear P2VP.	136
B.15	NMR spectrum for BB ₁₀ + Linear P2VP.	136

B.16 NMR spectrum for BB ₅ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	137
B.17 NMR spectrum for BB ₆ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	138
B.18 NMR spectrum for BB ₇ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	139
B.19 NMR spectrum for BB ₈ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	140
B.20 NMR spectrum for BB ₉ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.	141

B.21 NMR spectrum for BB ₁₀ . The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M _n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer..	142
B.22 GPC for precursor bottlebrush (a) B _{5,6,7} (b) B _{8,9,10} .	143
B.23 GPC for (a) P(S-co-2VP) ₁ (b).P(S-co-2VP) ₂ (a) P(S-co-2VP) ₃ (a) P(S-co-2VP) ₄ .	144
B.24 GPC for P(S-co-2VP) ₅ .	144
B.25 GPC for (a) BB ₅ (b) BB ₆ (c) BB ₇	145
B.26 GPC for (a) BB ₈ (b) BB ₉ (c) BB ₁₀	146
B.27 OWRK fits for (a) P(S-co-2VP) ₁ as-cast (b).P(S-co-2VP) ₁ annealed (c) BB ₁₀ as-cast (d) BB ₁₀ annealed.	147
B.28 NMR spectrum for NB-CTA at (t=0). The peak (a, 2H, 6.1 ppm) indicates presence of norbornene in NB-CTA.	148
B.29 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=1). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	149
B.30 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=2). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	150
B.31 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=3). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	151
B.32 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=4). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	152

B.33 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=5). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	153
B.34 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=7.5). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	154
B.35 NMR spectrum for homopolymerization of NB-CTA bottlebrush at (t=10). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.	155
B.36 NMR spectrum for NB-PS at (t=0). The disappearance of peak (b, 2H, 6.1 ppm) was monitored to get conversion of NB-PS macromonomer to bottlebrushes.. . . .	156
B.37 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=1). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 35% conversion of NB-PS to bottlebrush).	157
B.38 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=3). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 55% conversion of NB-PS to bottlebrush).	158
B.39 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=4). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 60% conversion of NB-PS to bottlebrush).	159
B.40 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=5). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 71% conversion of NB-PS to bottlebrush).	160
B.41 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=7.5). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 85% conversion of NB-PS to bottlebrush).	161

B.42 NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=10). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 89% conversion of NB-PS to bottlebrush).	162
B.43 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=0.5). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.	163
B.44 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=1). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.	164
B.45 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=2). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.. . . .	165
B.46 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=3). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.	166
B.47 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=4). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.. . . .	167
B.48 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=5). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.. . . .	168
B.49 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=7.5). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.. . . .	169
B.50 NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at (t=10). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.. . . .	170

Chapter 1

Introduction

Surface modification is a process utilized universally to convey either short or long-term properties with efficient functionality in polymers. This type of surface treatment widens the scope of applications for polymers by augmenting the existing tunable bulk properties of the materials, such as density, tensile strength, and elasticity.[1] A wide range of processes can be used to implement these surface treatments, the most commonly used method is by changing surface energy.[2] Modulating surface energy can alter properties such as wetting, absorption, and adhesive strength, where a polymer's surface energy is reconditioned by adding functional groups to the surface and treating polymer surfaces with various treatment processes such as physical, chemical, light-based or ionic.[3]

Various methods exist to modify polymer surfaces, usually via physical or chemical routes. Surface modification employed via physical methods are straightforward, easily scalable and very cost-effective. As physical methods for surface modification do not involve the use of any chemicals they are also eco-friendly and polymer surfaces obtained after physical treatments are generally resistant to abrasion and are more robust as compared to other methods of surface modification. When conventional physical treatment methods are inadequate to meet the required properties, surface modification using chemicals is appropriate. The majority of chemical treatment

methods involve wet procedures in which surfaces are either submerged or coated with a chemical to alter the properties at the surface. For example, using potassium iodide-iodine solution on Nylon’s surface, where adhesion is increased by increasing the crystalline nature and molecular weight.[4] Surface modification techniques have been used commonly in commercial fields to achieve properties like anti-fouling, adhesion or wettability.[5, 6] But these methods does have limitations such as a requirement of additional processing steps, long term stability issues for coatings.

A unique approach for surface modification is via preferential segregation of additives when blended with other polymers, In a polymer blend system one constituent is enriched at the surface. This technique has various benefits when compared to other techniques. Due to enrichment, this method can be applied with a slightest amount of additive. Moreover, as the additives are anchored to the surface with entanglements they have extended durability.[7] In some specific cases, if the additive is removed from the surface, segregation of more additive from the linear host matrix is possible. Hence, in cases where large damage occurs on the surface, restoration of the surface is possible. Furthermore, as compared to polymer grafting, surface modification from this technique is uniform.[8]

Surface segregation is driven thermodynamically, and is usually controlled by entropic and enthalpic driving forces. Enthalpic contributions arises due to the fact that constituent with low-cohesive energy density is attracted towards the low-energy surface, as the lower energy constituent by enrichment decreases the overall surface energy of the system.[9] On the other hand, entropic contributions are controlled by molecular weight, stiffness, architecture of the polymer and loss of configurational entropy near the surface.[10, 11]

Enthalpic Effects: In polymer blends, surface segregation can be driven by enthalpic effects controlled by monomer chemistry. It has been shown that even the inclusion of a small difference in chemical structure among the constituent of a binary blend can affect the surface segregation dramatically. This small difference in

the surface energy of components leads to an enthalpic preference of one component at the interface in such a way that the component with the lower cohesive energy enriches the surface. Usually, the component with lower cohesive energy also has a lower surface energy. This behaviour has been shown in different systems. For example, Jones and co-workers showed that when high-molecular weight isotopic blends of polystyrene (PS) and deuterated polystyrene (dPS) are blended together, surface enrichment of d-PS is observed which is driven by the difference in surface energy of isotopic origin.[12] In another work by the same authors, when isotopic polymers of poly(ethylenepropylene) (PEP) and perdeuterated poly(ethylenepropylene) (d-PEP) with a similar degree of polymerization ($N = N_{(\text{deuterated})} = 2286$) are blended a similar behaviour is observed.[13] Hence, when surface segregation in blends of polymers is controlled by enthalpic effects, polymer with lower surface energy would enrich the surface. Usually lower surface energy polymers are less polar/less hydrophilic so enrichment of the component with lower surface energy makes the surface more hydrophobic, which is a limitation when surface segregation is controlled by enthalpic preference at the surface.

Entropic Effects: When monomer chemistry in all the constituents of a polymer blend is the same, chain length and architecture of the polymers become relevant. For example, when linear polymers have a distribution of chain lengths, the linear polymer with shortest chains are attracted to the surface. In blends of branched and linear polymers, the branched polymer is usually attracted to the surface. This behaviour in blends arise from entropic effects as the chain ends are preferred on the surface.[14–16] In blends of branched and linear polymers, branched polymers could have different chemistry but strong entropic attractions of branched polymers to the surface can overcome the enthalpic preferences and cause surface enrichment of branched polymers at the surface.

In the field of polymer science, a pertinent question has been to what limit entropic effects can compensate for enthalpic effects leading to enrichment of high

energy constituent on the surface and induce a "wetting reversal". There have been some examples of experimental work performed to examine this point in bidisperse, miscible blends of linear polymers. In these model systems, when the gain in surface energy gain " $\Delta\gamma$ " is almost insignificant ($\sim 0.2\%$) [17] a wetting reversal is archived but when the gain in surface energy is around ($\Delta\gamma \sim 4 - 7\%$) wetting reversal is unfavourable.[18] When it comes to miscible blends of high energy branched polymers and low energy linear polymers with a $\Delta\gamma$ approximately 4%, enrichment of the high energy polymers is observed at the surface.[19]

Bottlebrush polymers are a class of highly branched polymers with densely grafted side chains to a linear backbone which can be used as surface-active polymer additives. Synthesis of these bottlebrush polymers is a simple and easy process which is compatible with a wide range of monomer chemistries.[20, 21] Our group and collaborators have studied a variety of nearly-athermal blends of bottlebrush polymers and linear polystyrene and have shown that surface segregation in these blends depends on relative length of linear chains of linear matrix (N_m) and side chains of bottlebrush (N_{sc}). Especially, when the ratio of $N_m/N_{sc} > 2$. Then, the bottlebrush polymers have chain ends larger than linear polymer and hence, they enrich the free surface. This same rule also apply to conditions for surface segregation in thermal systems when the surface energy of bottlebrush polymers is either higher or lower as compared to the surface energy of linear polymers.[8, 22, 23]

Chapter 4 describes the design of "high-energy" bottlebrush copolymers as surface active additives for a linear host matrix with a unique architecture and tunable chemistry. The bottlebrush copolymers are synthesized with a mixture of side chains containing "high energy" poly (2-vinylpyridine) (P2VP) chains, and "compatibilizing" polystyrene (PS) side chains. Using surface energy measurements it is discovered that the surface energy gain was approximately ($\Delta\gamma = 15\%$) which is maximum surface energy attained in this study. As seen from athermal blends, $N_m/N_{sc} > 2$ is required for enrichment of bottlebrush polymers at the surface. But this condition alone is not sufficient to tell if the high energy surface will be stable

through thermal annealing. Hence, we came up with conditions to suppress dewetting for bottlebrush copolymer/linear polymers interface. According to these conditions, an upper limit of N_m was found along with bottlebrush polymers having high energy side chain lengths shorter than the compatibilizing side chains.

Chapter 5 describes our efforts in studying the factors controlling the surface energy of bottlebrush copolymers. P2VP and PS have a surface energy of approximately 53 mN/m and 42 mN/m respectively. And bottlebrush copolymers from the first study in Chapter 4 where all the bottlebrush copolymers have 60% and 40% side chains of P2VP and PS respectively had a surface energy of approximately 48 mN/m. Changing the mole percent of P2VP in these bottlebrushes did not effect the surface energy. This begs the question if the surface energy is controlled by number of repeat units of each constituent present in the bottlebrush or mole percent of each constituent. To further explore this, surface energies of bottlebrush copolymers with 30% P2VP side chains, 60% side chains P2VP, 50% side chains P2VP and linear copolymers with varying concentration of 2-vinylpyridine (2VP) and styrene (S) were compared with varying repeat units and mole percent of 2VP. Along with this, the microstructures of bottlebrush copolymers were also studied. As the anchor groups used in side chains of PS and P2VP in bottlebrush copolymers are different, they should react at different rates. Kinetic studies were performed on each homopolymers and copolymer (precursor bottlebrush) to determine if the side-chain sequence was closer to random or gradient.

Chapter 2

Synthesis

This chapter describes major synthesis methods used to synthesize linear and bottlebrush polymers throughout the duration of my research. Reversible addition-fragmentation chain transfer (RAFT) polymerization was used to synthesize most of the linear polymers in my studies, including macromonomers and linear copolymers. For the majority of bottlebrush copolymer synthesis, a hybrid approach of "grafting through" ring-opening metathesis polymerization (ROMP) followed by a "grafting from" was utilized. The background and basic functioning of RAFT and ROMP polymerization are discussed below.

2.1 RAFT polymerization

One of the most commonly used methods for commercial production of high molecular-weight polymers is radical polymerization. There are major factors responsible for this technique's leading position such as reaction conditions and wide applicability to monomers. As compared to other competitive technologies, radical polymerization is inexpensive and easy to implement, but the process has some limitations regarding the degree of control that can be implemented on the architecture of macromolecules, composition of copolymers, and molecular weight distribution.[24, 25] These limitations were addressed by techniques such as reversible

deactivation radical polymerization (RDRP), which is also known as controlled or living radical polymerization. While retaining the benefits from conventional radical polymerization, RDRP also provides other attributes such as simultaneous growth of all chains, preservation of end group functionality, and can be used to make block copolymers by addition of further monomers.

In the past 20 years, there has been an immense increase in interest towards reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerization was first developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) in the mid-1990s.[26] It is a powerful and widely recognized polymerization technique that is widely assumed beyond polymer synthesis labs as a method to create materials with a wide range of applications such as materials science, medicine, etc. RAFT can be used for making a broad range of architectures [27] such as stars [28], and networks.[29]

An ideal living polymerization has specific attributes such as 1) All chains are initiated at the same time hence all chains grow at similar rate and have a narrow distribution of molecular-weight, 2) Number average molecular weight (M_n) is a linear function of conversion and monomer addition continues until all the monomers have been consumed, 3) Block copolymers can be prepared by sequential monomer addition, and 4) Stoichiometry of reaction can be utilized to control the molecular weight of the polymer. RAFT polymerization has some of the advantages as a living polymerization such as 1) It produces controlled molecular weight and very narrow molecular weight distribution, 2) Linear increase in molecular weight with increase in conversion and 3) As the number of dead chains in RAFT polymerization is dictated by the amount of radical species from initiator, independent of monomer conversion. Block copolymers with 100% monomer conversion can be obtained.

A general mechanism for RAFT polymerization is depicted in Figure 2.1.[30] Usually, a RAFT polymerization is initiated by a free radical source such as 2,2'-azobis(isobutyronitrile) (AIBN) which is a thermal initiator as shown in Step I of Figure 2.1. This radical from Step I reacts with the monomer molecule (M) to give a

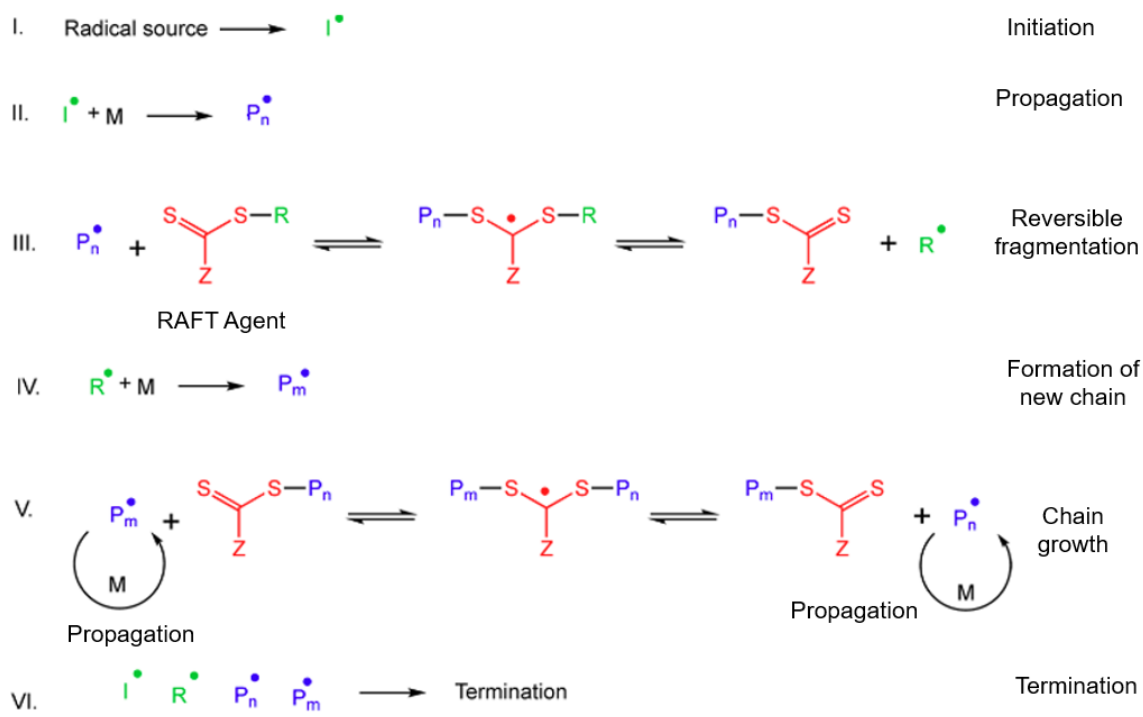


Figure 2.1: Mechanism of RAFT polymerization. Image reproduced from reference [30].

propagating radical chain of length (n), which is in the active form P_n^* as shown in Step II of Figure 2.1. This propagating radical chain of length (n) can couple on to the RAFT agent to form an intermediate radical which can undergo fragmentation reaction in either direction to yield the reactants or ($R\cdot$) and polymeric RAFT agent ($S=C(Z)S-(P_n)$) as shown in Step III of Figure 2.1. The leaving ($R\cdot$) species from Step III can react with monomer molecules (M) to start another polymeric chain P_m^* as shown in Step IV of Figure 2.1. The growing polymer chains P_m^* can react with dormant polymer to release P_n^* as a radical for further opportunity to grow as shown in Step V of Figure 2.1. Finally, active chains react to form dead chains via various forms of termination (coupling, disproportionation etc.)

A vast variety of monomers can be polymerized using RAFT polymerization. Almost all the vinyl monomers can be categorized in two groups depending on their reactivities, these two categories are "more activated" monomers (MAMs) and "less activated" monomers (LAMs). MAMs usually have a vinyl group conjugated to either a double bond (isoprene), aromatic ring (styrene), carbonyl group ((meth) acrylate), or a nitrile group (acrylonitrile). On the other hand, LAMs usually have a double bond conjugated to either a nitrogen (N-vinylpyrrolidone), oxygen (vinyl acetate), halogen (vinyl chloride) or saturated carbons. RAFT polymerization imparts very good control over almost all the monomers that can be polymerized via free radical polymerization, some exceptions might include monomers with functionality that could react with the thiocarbonylthio group present in the RAFT agent to undergo unwanted side reactions.

Selection of the RAFT agent is an important step for successful RAFT polymerization. Some guidelines have been proposed for the selection of RAFT agents such that the polymerization is well controlled with most monomers to provide low to minimal retardation and a higher fraction of living chains.[32] Figure 2.2 shows the required properties for a RAFT agent. The effectiveness of RAFT relies on the monomer subjected to polymerization and is determined by the activating group 'Z' and the leaving radical group 'R's properties. The reactivity of the $C=S$

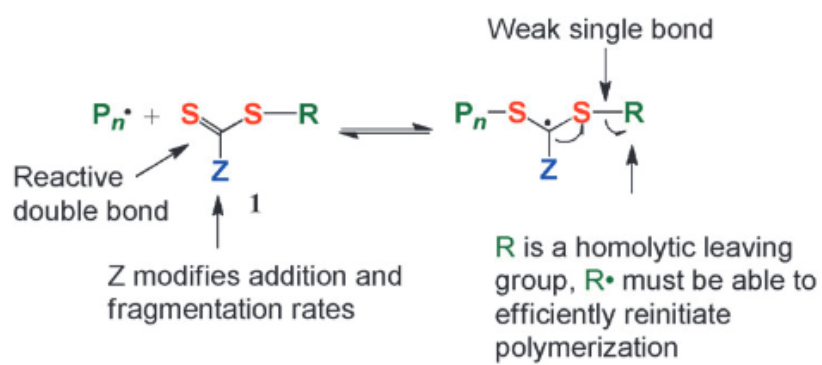


Figure 2.2: Typical RAFT agent with required properties of (R) and (Z) group. Image reproduced from reference [31].

bond towards the addition of a radical is governed by the Z-group and hence, it governs the stability of the intermediate radical. On the other hand, the function of the R-group in RAFT polymerization is more subtle. R-group affects the RAFT polymerization by (a) successive fragmentation from the intermediate present in the reaction, for fragmentation R-group has to be a good leaving group, (b) propagation, after fragmentation the R-group has to rapidly re-initiated propagation to make sure all the chains are initiated in same time interval and narrow molecular weight is obtained. Usually, good R-groups have a structure that resembles thermal initiators such as AIBN.

2.2 Ring Opening Metathesis Polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP) has a very long and rich history since the early stage development of the Ziegler-Natta catalyst, the very first demonstration of ring-opening polymerization of cyclic olefins was reported in 1960 as a coordination polymerization of norbornene using TiCl_4 .^[33] The first reaction recognized as metathesis polymerization was reported by Calderon et al. in 1967.^[34] The first ROMP with a well-defined catalyst was reported in 1976 by Katz et al.^[35]

ROMP polymerization is a powerful and broadly applicable method used for synthesis of macro-molecular materials.^[36] ROMP is a type of chain-growth polymerization in which cyclic olefins containing high-oxidation-state transition-metal alkylidenes either mono-, bi-, or multicyclic go through ring opening to form a polymer chain as shown in Figure 2.3. ROMP is a chain growth polymerization based on olefin metathesis, which belongs together with group transfer and Ziegler-Natta-type of polymerization. ROMP has a unique mechanism based on olefin metathesis in which a metal-mediated carbon-carbon double bond exchange process takes place. Consequently, unsaturation associated with the monomer remains even

after conversion to polymer. This is an important distinction ROMP has as compared to a typical olefin addition polymerization (for example: conversion of ethylene to polyethylene).

Figure 2.3 shows a general mechanism of ROMP.[38] Reaction begins when the metal alkylidene complex coordinates with the cyclic olefin and forms a four-membered metallacyclobutane from [2+2]-cycloaddition. The intermediate formed after the coordination step, which is essentially the start of the polymer chain, forms a metal alkylidene after undergoing cyclo-reversion. After propagation, even though the size of the resulting complex has increased resulting from successive additions, the reactivity of the complex towards cyclic olefin remains the same as compared to the initiator. Hence, the same reactions are repeated until all the monomers present in the reaction are consumed or reach an equilibrium, or the reaction is quenched by adding a very small amount of chemical to deactivate the catalyst.[39]

Thermodynamically, ROMP is driven by the release in ring strain, hence having monomers with high ring-strain energy is favorable such as high-strained monocyclic alkenes and polycyclic alkenes. Norbornene and its derivatives are especially widely recognized as good monomers for ROMP. Most of the monocyclic alkenes can be used as monomers for metathesis reaction, but when it comes to monocyclic olefins, from 4 to 8-membered cyclic olefins except cyclohexane derivatives are favorable when used as monomers for ROMP. This results due to the lack of ring-strain in the 6-membered ring, hence cyclohexanes and their derivatives are thermodynamically unfavorable for ROMP. In a 4-membered ring, cyclobutane and its derivatives have a higher ring strain but have disadvantages in the synthesis of substituted monomers. In 5- and 7-membered rings, cyclopentane and cycloheptane derivatives have a similar ring strain, and the reactivity is poor as compared to the reactivity of an 8-membered ring during ROMP. The 8-membered monocyclic olefin ring and its derivatives are most popular for ROMP. Numerous examples can be found for ROMP of cyclooctene since it was first reported in 1966 by Natta.

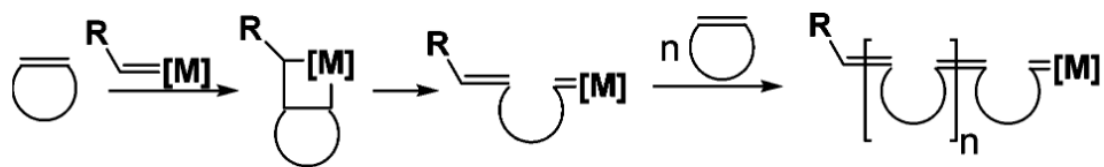


Figure 2.3: General mechanism of a ring-opening metathesis polymerization (ROMP). Image reproduced from reference [37].

2.2.1 Bottlebrush Polymers

Bottlebrush polymers are highly branched polymers with polymeric side chains attached to densely grafted backbone chains, as shown in 2.4. These polymers are promising in applications which rely on densely packed polymeric chains and highly extended macromolecules. Some examples include drug delivery, polymer photonics, and stimuli-responsive surfaces. There are three general techniques for synthesizing bottlebrush polymers including grafting from [40], grafting to, and grafting through [36, 41] as shown in Figure 2.5.

Grafting from: Grafting from technique for synthesis begins with the formation of a bottlebrush backbone containing a macroinitiator. These initiation sites are then used to initiate the side-chain polymerization, as shown in Figure 2.5. This method enables the formation of bottlebrush polymers with high grafting density and narrow molecular weights.[40] But it won't provide perfectly grafted polymers because of the backbone not initiating completely. Also, due to the steric factors side chain length of the bottlebrush polymer will be smaller as compared with other methods such as grafting-to and grafting-through.[42]

Grafting to: Grafting to technique for bottlebrush synthesis involves a reaction between end-functionalized monomers and a polymer backbone attached to reactive groups. To synthesize bottlebrush polymers, the reactive groups on the backbone are coupled with end groups present on end-functionalized monomers, as shown in Figure 2.5. The unique feature of "grafting-to" technique is that both polymers can be synthesized independently. According to the respective monomer chemistry of side chains and backbone, separate mechanisms and characterization can be utilized before coupling. However, low grafting density is usually observed because of steric effects between side chains. Hence, excess side chains are added to improve grafting density.[42, 43]

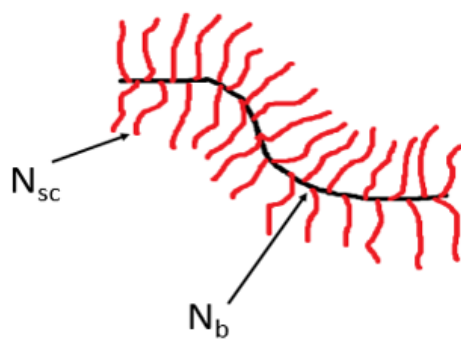


Figure 2.4: A simple schematic of bottlebrush polymer where N_{sc} is side chain degree of polymerization and N_b is backbone degree of polymerization.

Grafting through: Grafting through technique for bottlebrush synthesis involves first synthesizing the macromonomers with terminal functionality. These reactive groups at the chain ends can then be reacted to form bottlebrush polymers. This technique allows synthesis of bottlebrush polymers with high grafting density and well-defined side chains.[42] Usually, the grafting-through method is employed for ROMP of macromonomers (MMs) containing norbornene end groups.[44, 45] First, macromonomers functionalized with norbornene are prepared by norbornene anhydride derivatives [46] or imidization or esterification of norbornene carboxylic acid.[47] During ROMP, macromonomers terminated with norbornene mediate with highly active olefin metathesis catalyst to afford narrowly dispersed bottlebrush polymers.

2.2.2 Research methodology and alternate approach for synthesizing bottlebrush polymers

Most commonly, bottlebrush polymers are synthesized via ring-opening metathesis polymerization of norbornene terminated macromonomers in the presence of Grubbs third generation (G3) catalyst using the "grafting through" approach. A significant amount of experiments performed during this research work involve working with polymers containing poly (2-vinylpyridine) (P2VP) and polystyrene (PS). The model system is based on linear PS as the host polymer and bottlebrush copolymer additive with side chains of P2VP and PS. However, P2VP chains has a pendant nitrogen atoms with a lone electron pair in the aromatic ring.[48] ROMP of pyridine-containing macromonomers is not feasible as they interact with the G3 catalyst. These challenges during synthesis are addressed by employing a combination of synthesis procedures.[20, 49] A recent work by Kim et al. demonstrated the synthesis of bottlebrush block copolymers with pyridine moieties, using a procedure with a combination of "grafting through" and "grafting to" methods.[20]

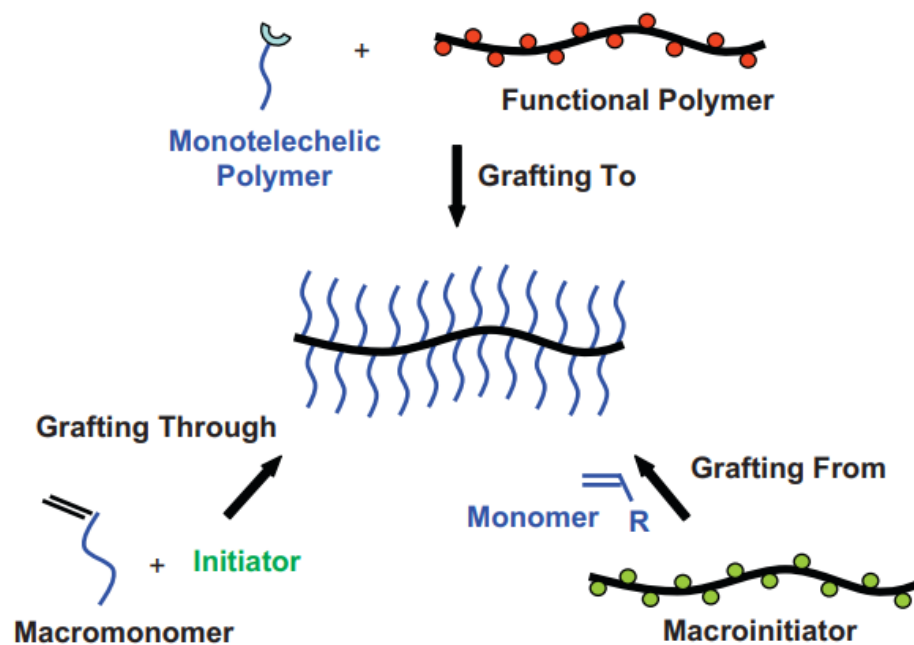


Figure 2.5: Representation of a grafting-to, grafting-through and grafting-from reaction to synthesize bottlebrush polymers. Image reproduced from reference [42].

In our research, we devised a hybrid approach for the synthesis of P2VP-*co*-PS bottlebrush copolymers. This approach combines "grafting through" and "grafting from" methods, as shown in Figure 2.6. First, ROMP was performed on norbornene-functionalized polystyrene (NB-PS) and norbornene-functionalized chain transfer agent (NB-CTA), then RAFT polymerization was performed on precursor bottlebrush PS-*co*-CTA to grow P2VP chains. Kinetic studies were performed on NB-CTA, NB-PS, and copolymers of NB-CTA and NB-PS to investigate the microstructure of bottlebrush copolymers using a G3 catalyst. Unfortunately, in the presence of G3 catalyst, the homopolymerization of NB-CTA and copolymerization of NB-CTA and NB-PS were both very fast and could not be quantified. Hence, these studies provide no information on the microstructure of the bottlebrush. To further study the kinetics, the reaction was slowed down by decreasing the concentration of G3 in NB-CTA homopolymerization as described in Chapter 5.

2.2.3 Significance of the Anchor Group in Ring-Opening Metathesis Polymerization

Product from ROMP grafting through reaction places the carbonyl group in close vicinity of the Ru center in propagating alkylidene state. Due to the close proximity of the carbonyl group to the metal center, activity of the ruthenium complex is affected. This can lead to the formation of stable chelates, which might isolate the catalyst and make it ineffective.[50] When using Grubbs third-generation catalyst (G3) during ROMP it has been observed to cause retardation and effect rate of propagation.[51]

Radzinski et al. also observed a difference in the rate of propagation when the chemical structure of anchor groups was changed.[45] To study the effect of anchor groups, they prepared PS macromonomers with three different components connecting polymer units with chain ends terminated with norbornene. A general scheme XP_y was adopted to name macromonomers, such that X = anchor group present in the macromonomer, P = repeat unit of monomer either styrene (S) or

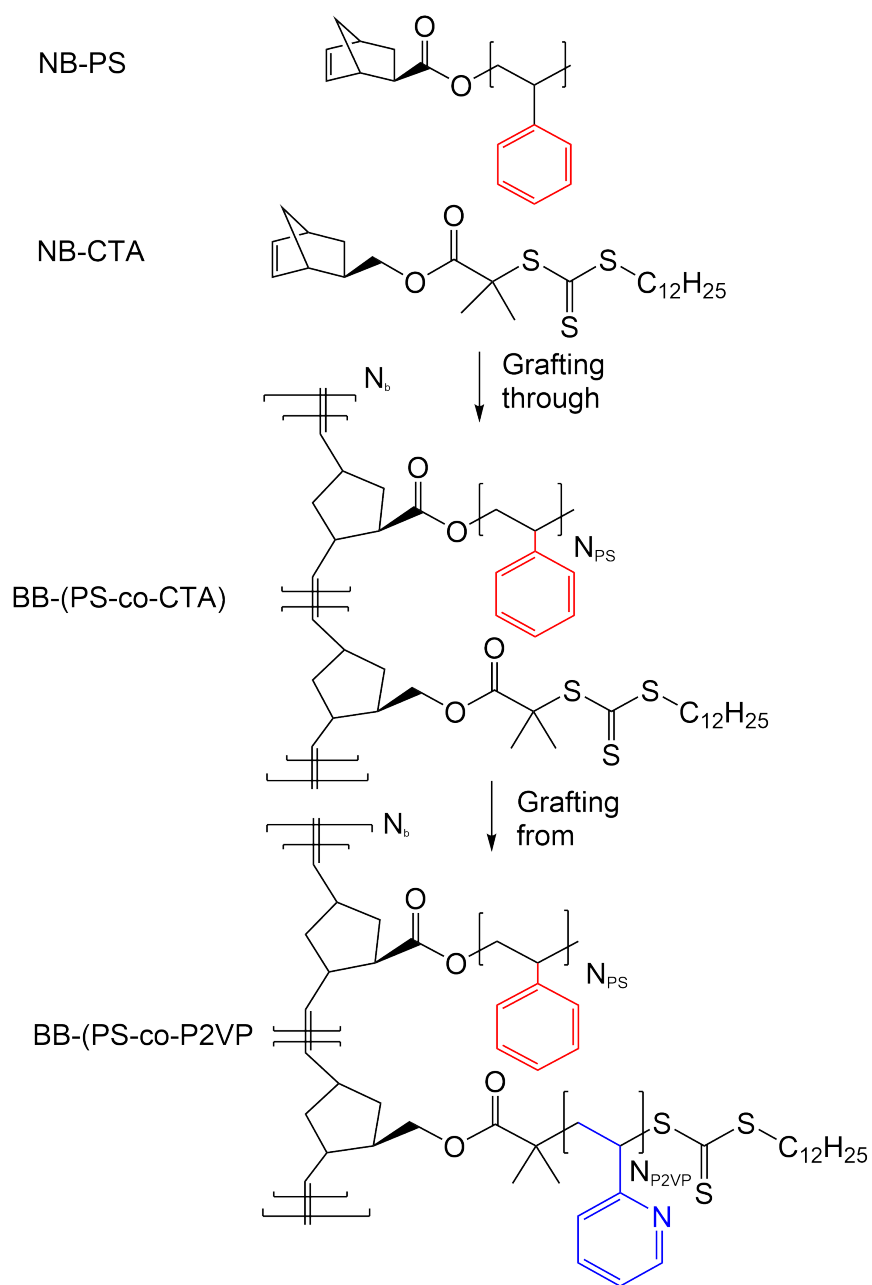


Figure 2.6: Scheme for the synthesis of P2VP/PS bottlebrush copolymers via a combination of "grafting through" and "grafting from" methods.

Lactide (L) and y = molecular weight of the macromonomer in Figure 2.7. For example, nomenclature $2L_{3k}$ represents the 2nd anchor group, with a polylactide chain of molecular weight 3 kDa. The three anchor groups selected for the study were widely used and also provided varying proximity of imide and ester carbonyl groups to the Ru metal center. A kinetic study was performed on macromonomers with all three anchor groups. ^1H Nuclear magnetic resonance (NMR) spectroscopy and size-exclusion chromatography (SEC) was performed to get the conversion. Using this conversion, half-lives and rate constants were obtained. Figure 2.8 (a) and (b) show results of kinetic studies from ^1H NMR and SEC respectively. The results obtained from both characterization techniques complimented each other as the trend of the relative rate of propagation observed for anchor groups was $1 > 2 > 3$. In our research project, the bottlebrush copolymers side chain (PS and P2VP) have different anchor groups as observed from the product in Figure 2.6. Comparing the anchor groups used by Radzinski and coworkers with our work, the PS side chains have anchor group number 2, and P2VP side chains have anchor group number 1. Hence, we would expect anchor group 1 to react much faster than anchor group 2nd, which makes monitoring the kinetics of the reaction difficult. These differences in the rate of propagation between anchor group 1 and anchor 2 can also be attributed to the steric effects associated with relative bulkiness PS and CTA chains as shown in Figure 2.6.

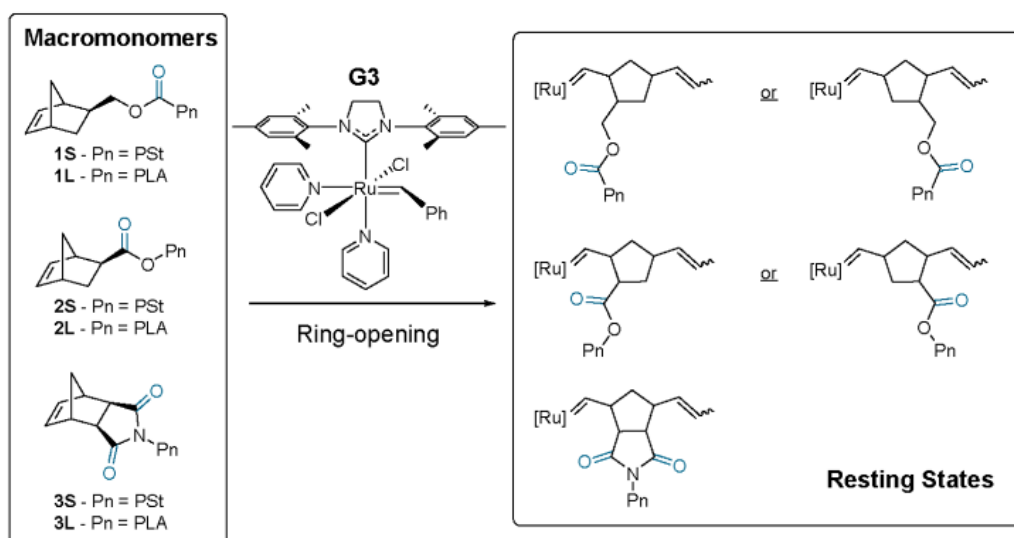


Figure 2.7: Structures for three macromonomers (MMs) used by Radzinski and coworkers with three different anchor groups. Depicting possible chelation between the Ru metal center and carbonyl oxygen present in the anchor group along with regio-isomers unlikely to form chelates. Image reproduced from reference [45].

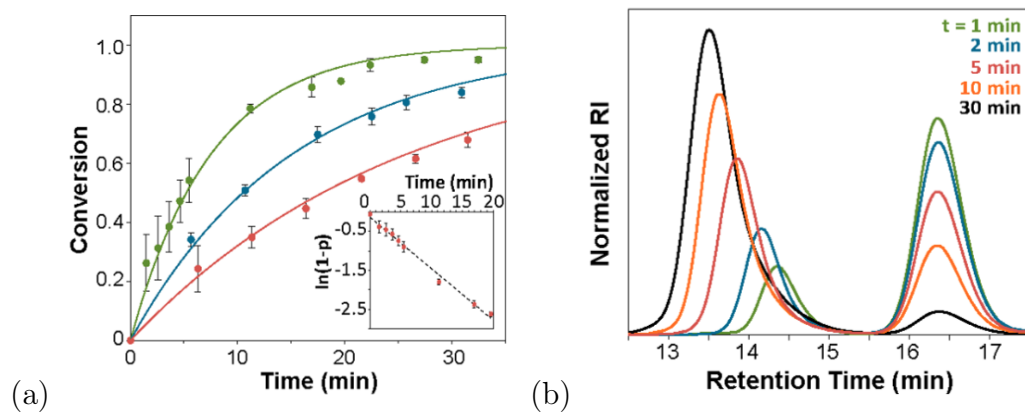


Figure 2.8: (a). Results for kinetic analysis for ROMP of polystyrene MMs ($M_w = 3$ kDa) where $[MM]/[G3]$ ratio = 100 and concentration 50 mg/ml (green circle = 1S_{3k}, blue circle = 2S_{3k} and red circles = 3S_{3k}) (b). SEC traces for the kinetic study for PS MM ($t = 1, 2, 5, 10$ and 30 min) for 1S_{3k}. Image reproduced from reference [45].

Chapter 3

Methods

This chapter details characterization methods such as surface energy measurement and time-of-flight secondary ion mass spectrometry (ToF-SIMS), which have been integral to this research project. The model system for one of my studies is linear polystyrene (PS) with bottlebrush poly(2-vinylpyridine)-co-polystyrene (BB-P2VP-*co*-PS) as an additive. ToF-SIMS has been critical in detecting the enrichment of bottlebrushes, obtaining depth profiles and 3D images. Surface energy measurements have complimented the results that were observed from ToF-SIMS. In Chapter 4, I described my efforts to achieve wetting reversal in blends of BB-(P2VP-*co*-PS) with linear PS. I also used surface energy measurements to confirm a 15% increase in the surface energy of bottlebrush as compared to surface energy of linear host matrix and performed ToF-SIMS depth profile. In Chapter 5, I again used surface energy measurements to establish which design attributes control the surface energy of the BB-(P2VP-*co*-PS).

3.1 Surface Energy Measurement

Surface tension results from an imbalance in inter-molecular forces that act between the molecules. As illustrated in Figure 3.1, forces work differently on the molecules present in the bulk and the liquid's surface. Molecules in bulk liquid are in a stable

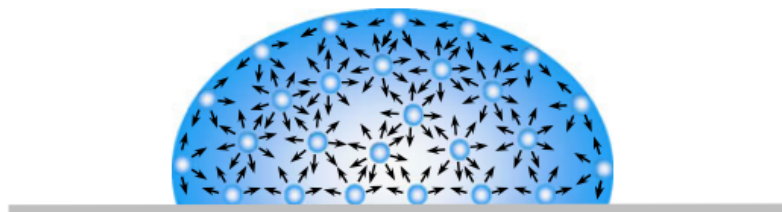


Figure 3.1: Imbalance in inter-molecular forces between molecules at the bulk or surface. Image reproduced from reference [52].

state because these molecules have an equal cohesive force acting equally in all directions. However, molecules at the surface have a force imbalance as the surface only has intermolecular forces acting inwards, pulling these molecules inwards. Hence, the liquid's surface minimizes itself to the smallest surface area possible, giving rise to surface tension. As compared to the surface tension of liquids, surface tension of solids is known as surface free energy.[52] The force required to pull a unit length is known as surface tension and the energy required per unit area to increase size of a surface is known as surface energy. Typically, there are two types of solids namely high-energy solids and low-energy solids. Depending on the nature of these solids the energy is determined from their own bulk nature. Solids which are hard in nature consist of chemical bonds (such as metallic, covalent or ionic bonds), these bonds hold themselves together and are very strong. To break these solids, a considerably high amount of energy is required and hence, they are labeled "high-energy". Some examples of these solids are metals, glasses and ceramics. On the other hand, other solids are connected together by physical forces (such as Van der Waals forces or hydrogen bonding) and consequently, they are labeled "low energy" because a small amount of energy is required to break these solids. Some examples of these types of solids are fluorocarbons and hydrocarbons.[53]

When a liquid droplet interacts with a solid surface, there are typically three interfaces to consider: liquid-solid, solid-vapor, and vapor-liquid surrounding the system. Figure 3.2 shows an image of the droplet edge meeting the solid surface. The three arrows represent the interfacial tensions at the three-phase boundary. When the liquid droplet is in an equilibrium state, a balance of forces can be written as shown:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta \quad (3.1)$$

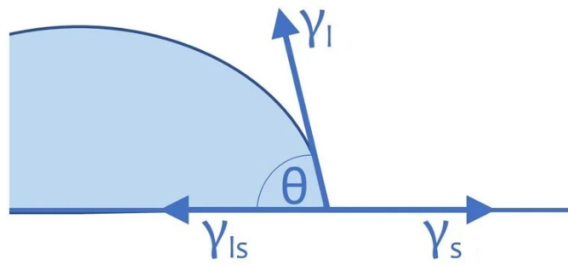


Figure 3.2: Equilibrium of forces during a liquid wetting a solid according to Young's equation. Image reproduced from reference [54].

Here, rearranging the above equation gives:

$$\cos \theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad (3.2)$$

The above equation 1.1 is also known as Young's equation [54] where γ_s is defined as surface free energy of the solid, γ_l is defined as surface tension of the liquid, γ_{sl} is defined as interfacial tension between the solid and liquid and θ is defined as the equilibrium contact angle. One of the underlying assumptions of Young's equations is, it considers a perfectly flat surface. Still, impurities and surface roughness can cause deviations in the measured equilibrium contact angle compared to the predicted Young's contact angle. Several methods can be used to calculate surface energy, one of the most widely used techniques is by measuring the static contact angle of reference liquids on a solid's surface by using sessile drop method.[55]

3.1.1 Contact Angle Measurement

A contact angle goniometer can be used to measure the static contact angle of reference liquid, the measurement typically involves two steps recording and analysis. Three basic components are required for this method: a light source, a camera and a stage. A schematic of the measurement process from contact angle goniometer is shown in Figure 3.3, first the stage is leveled to make sure the droplets of reference liquids on solid's surface do not move during the measurement. The solid surface on which the measurement will be performed is mounted on the stage. Using a syringe, a fixed amount of reference liquid is dispensed and deposited on the solid's surface mounted on the stage. The droplet of liquid formed on solid's surface is illuminated from behind, which can be recorded by the camera. An image of reference liquid droplet sitting on a solid surface is shown in 3.4. The video of reference liquid sitting on solid's surface is recorded for 60 seconds and analyzed using a code or software to determine the contact angle.

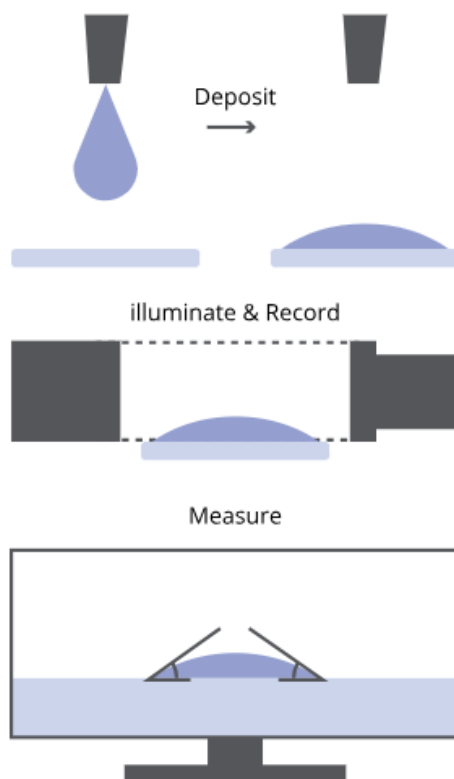


Figure 3.3: A brief overview of contact angle measurement process using a contact angle goniometer. Image reproduced from reference [56].

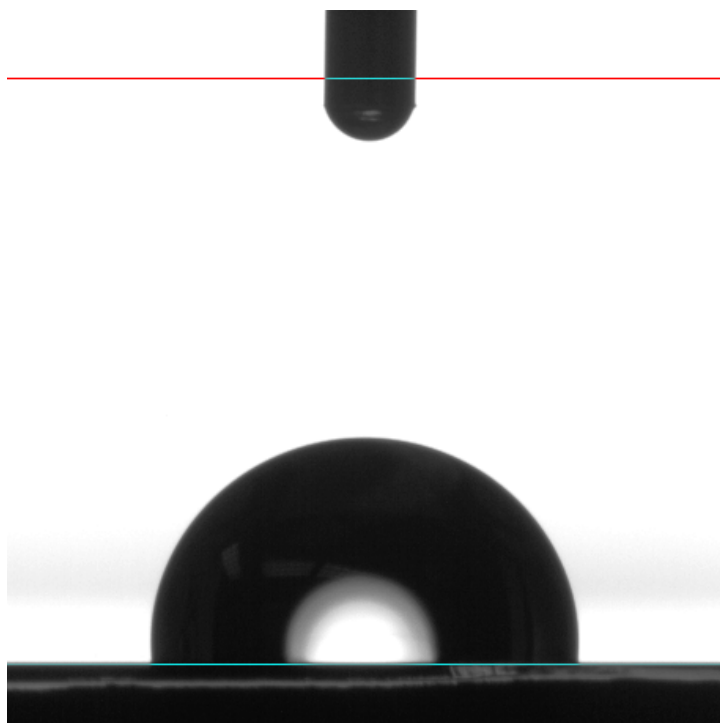


Figure 3.4: Image of a liquid's droplet with clear visible edges.

3.1.2 Models for solid-liquid interfacial energy measurement

The surface free energy of solids cannot be measured directly but can be measured indirectly by using static contact angles from sessile drop method. Many theoretical models have been developed to estimate surface free energy from contact angles. These models provide a relationship between the surface free energy of solids and the contact angles of reference liquids. Some of the most commonly used models are Zisman [57], Fowkes [58], Owens Wendt Rabel and Kaelbel (OWRK) [59] and Van Oss-Chaudhury Good (VGC) [60] model. All these methods are unique and have different attributes as they provide information on either total surface energy, all components of surface energy (dispersive, polar, or hydrogen bonding), or both. The biggest difference between these models arises from the treatment of molecular interactions. For example, Zisman model uses a single-component model and does not divide into polar and dispersive parts, OWRK model divides surface free energy into polar and dispersive parts and Van Oss-Chaudhry Good model further divides polar component into acid and base.[61] Throughout this project, OWRK method has been used for all surface energy measurements.

Choosing reference liquids for surface energy measurement is very important, as a wide range of dispersive or polar fluids should be selected. The total surface tension of liquid can be broken into a polar and dispersive component. Usually, the polar component accounts for interactions between permanent dipoles and also, interactions between permanent and induced dipoles. The dispersive component accounts for Van der Waals forces present between all the molecules. Some popular reference liquids used are water, diiodomethane, ethylene glycol, glycerol, dimethyl sulfoxide or thiodiglycol, as they span over all the surface energies found on common materials.

Most of the polymers synthesized during this study include repeat units of polystyrene (PS) or poly (2-vinylpyridine) (P2VP). P2VP is suspected to have higher energy than the host polystyrene. While measuring contact angle with polymers containing high energy P2VP such as linear P2VP, BB-(P2VP-*co*-PS), and linear

copolymers of (PS/P2VP). Contact angle with water was omitted because water can hydrogen bond with pyridine. Hence, fluids which undergo hydrogen-bonding with the polymer must be avoided. For instance, the contact angle of water and ethylene glycol was omitted for linear P2VP films, and the contact angle with water was omitted for BB-(P2VP-*co*-PS) films.

OWRK model: OWRK is a standard model for surface free energy calculation of a solid using contact angles with several test fluids. Therefore, total surface free energy is divided in two parts, polar and dispersive components. As observed from earlier Equation 3.1, which is known as Young's equation, a relationship between contact angle θ , surface tension of the liquid (γ_l), interfacial tension between solid and liquid (γ_{sl}) and surface free energy of the solid (γ_s) is found. To determine the surface free energy the variable (γ_s) must be determined. OWRK models (γ_{sl}) as the geometric mean of the polar and dispersive parts of the solid's surface free energy (γ_s) and liquid's surface tension (γ_l) Equation 3.3

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 \left(\sqrt{\gamma_s^d \cdot \gamma_l^d} + \sqrt{\gamma_s^p \cdot \gamma_l^p} \right) \quad (3.3)$$

We can obtain a linear equation in the form of $y = mx + c$ after substituting equation 3.3 in Young's equation, which results in:

$$\frac{\gamma_l \cdot (1 + \cos \theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \quad (3.4)$$

In the above Equation 3.4, terms y and x contain all the known quantities along with the measured contact angle. The required dispersive (γ_s^d) and polar part (γ_s^p) of the solids surface free energy can be obtained from the slope (m) and the intercept (b) respectively as there are two unknowns at least 2 liquids with known polar and dispersive parts are required. Using linear regression, these parameters can be obtained while using contact angles of at least 2 test liquids. However, a regression line from just two points does not provide us with any information about

the accuracy of the result. Hence, contact angle measurements with 3 or more test liquids are recommended for reliable surface-free energy.

3.2 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

3.2.1 Introduction

The properties of solids that interest us are controlled by composition at the surface or near-surface regions. Hence, understanding and having knowledge of the surface composition is of utmost significance. Utilizing modern surface analysis techniques is a critical step toward achieving those goals. One of these surface analysis techniques is ToF-SIMS. It is regarded as one of the most advanced and major analytical techniques that can provide information regarding molecular and elemental chemistry at the surface or near-surface regions.

While performing SIMS, a focused ion beam is utilized to bombard the surface. This results in the sputtering of various particles, such as protons, electrons, and atomic and molecular species. When ions in the primary beam collide with molecules near the top of the surface, transfer of kinetic energy takes place during sputtering and formation of secondary ions.[62] From all the sputtered particles, a very small fraction of total particles (typically less than 1%) are charged and are useful for analysis, the majority of remaining particles atomic and molecular species are neutral. These charged particles are called secondary ions, and are useful in mapping the chemistry of the surface under analysis.[63, 64]

A simple overview of a ToF-SIMS instrument is shown in Figure 3.5. ToF-SIMS instrument consists of a primary beam, a secondary beam (dual sputter gun), and a mass analyzer. The primary beam is used for analysis, which does not etch the surface significantly. However, pairing the primary beam with a secondary beam aids in etching the sample to obtain a depth profile. The function of the ToF mass analyzer

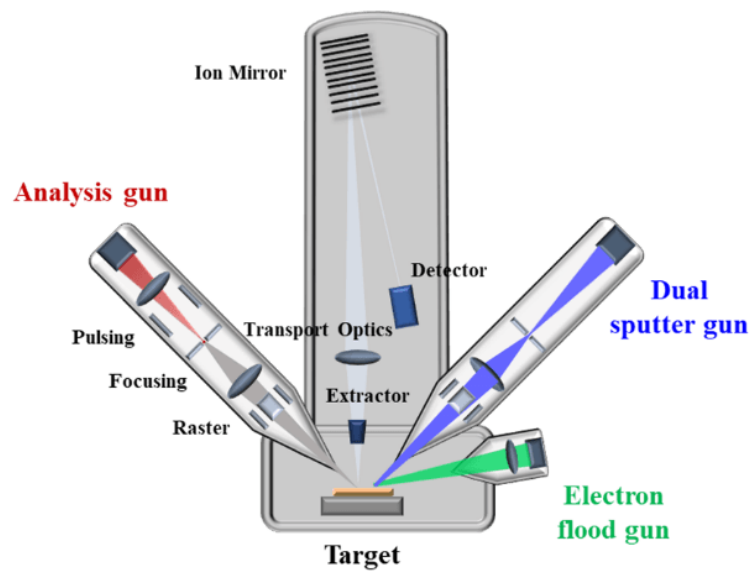


Figure 3.5: Overview of a ToF-SIMS instrument. Image reproduced from reference [65].

is to analyze the secondary ions accelerated by the instrument and store the (m/z) ratios, also known as mass-to-charge ratios. In addition, with its excellent mass-analyzing abilities, the ToF analyzer can differentiate ions.[66] Therefore, surface-sensitive analysis on a broad range of ions can be obtained by ToF-SIMS

3.2.2 Depth profiling of polymer blends

Typically, in polymer blends one constituent is enriched at the surface or interfaces. To detect this enrichment and quantify the surface excess, ToF-SIMS depth profiling can be used. There are numerous examples of depth profiling on blends of polymers in the literature. Mahoney et al. examined binary blends of poly (L-lactic acid) (PLLA) with an ABA-type block copolymer, also known as Pluronic surfactant where [A block = poly(ethylene oxide) and B block = poly(propylene oxide)] [67]. These blends are of very specific importance when it comes to protein drug delivery systems, as Pluronic surfactants increase the biocompatibility of the device but still retain the activity of the protein drug. Thin films of approximately 700 nm were prepared, and depth profiling was performed to detect the through-film composition of Pluronic throughout the film. From depth profiles, it was clear that Pluronic was enriched at the free surface, a region of depletion followed this region of Pluronic enrichment under the surface, followed by uniform composition in bulk and some enrichment at the film substrate interface.

Previous work from our group and collaborators at Rice University have performed depth profiling on thin films to detect surface enrichment in architecturally complex polymer blends.[22, 68] Bottlebrush polymers containing poly(methyl methacrylate (PMMA) and polystyrene (PS) side chains were used as an additive for either linear PMMA or linear PS as a commodity polymer. The important variables to keep in mind for this study were the degree of polymerization (DP) of the side chain of bottlebrushes (N_{sc}), DP of the bottlebrush backbone (N_b), and DP of linear PS or PMMA matrix (N_m). Previous work from our group and various studies in the

literature have successfully shown that when the ratio $N_m/N_{sc} > 2$, enrichment of bottlebrush polymers is observed. In the system mentioned above, thin films with 100 - 150 nm thickness were prepared. Using ToF-SIMS depth profiling, the distribution of bottlebrush copolymer additives was obtained. $C_2H_3O^+$, $C_7H_7^+$ and Si^+ ion signals were used to track PMMA, PS and silicon in thin films respectively. In linear PS matrix, the distribution of bottlebrush additives was obtained using ion intensity ratio $C_2H_3O^+/C_7H_7^+$ and similarly in linear PMMA matrix, the distribution of bottlebrush additives were obtained by using ion intensity ratio of $C_7H_7^+/C_2H_3O^+$. As-cast blend films of PS showed enrichment of bottlebrush copolymers at surface and substrate when $N_m/N_{sc} \geq 4.6$. As-cast blend films of PMMA showed enrichment of bottlebrush additives at the surface, and depletion at the silicon interface but enrichment near the silicon film interface when $N_m/N_{sc} \geq 2.8$.

3.2.3 Processing ToF-SIMS raw data

During the course of this research work, numerous TOF-SIMS depth profile analyses were performed. This section illustrates the procedure for getting depth profiles from raw data. The sample chosen for analysis contains high-energy BB-(P2VP-*co*-PS) blended with linear PS as a commodity polymer. Thin films with a thickness of approximately 500 nm were prepared, and ToF-SIMS was performed.

Example analysis of ToF-SIMS raw data for depth profiling: Raw data was obtained in the form of ion intensities of $C_7H_8N^+$, $C_7H_7^+$, and Si^+ , corresponding to P2VP, PS, and silicon, as a function of scan number. To convert scan number to depth, the Si^+ signal was plotted against scan number as shown in Figure 3.6 for BB-(P2VP-*co*-PS) blend with linear PS:

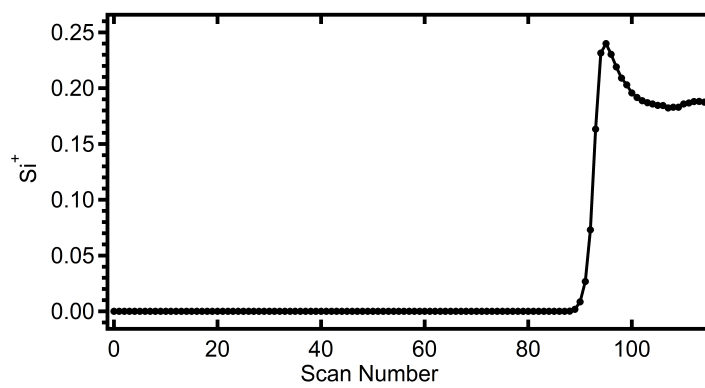


Figure 3.6: Si+ signal versus scan number plot for P2VP/PS bottlebrush blend with linear PS.

The scan number corresponding to the polymer/silicon interface (h) was determined by the mid-point of the rise in the Si^+ signal. Using the known film thickness from ellipsometry and the value for h , the scan number, was converted to depth by using equation 3.5

$$\text{depth} = \text{scan number} \times \text{film thickness}/h \quad (3.5)$$

The depth profile for blend mentioned above is shown in Figure 3.7, where the y-axis shows the relative signals for $m/z = 106.09$ ($\text{C}_7\text{H}_8\text{N}^+$) and 91.07 (C_7H_7^+) that are assigned to P2VP and PS, respectively. Finally, the depth axis was converted to a percent depth to facilitate comparison of samples having different thicknesses, as shown in Figure 3.8

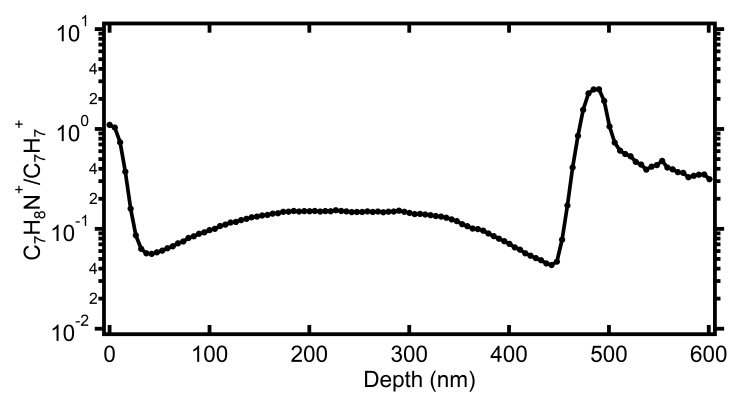


Figure 3.7: $C_7H_8N^+/C_7H_7^+$ signal ratio versus depth plot for P2VP/PS bottlebrush blend with linear PS.

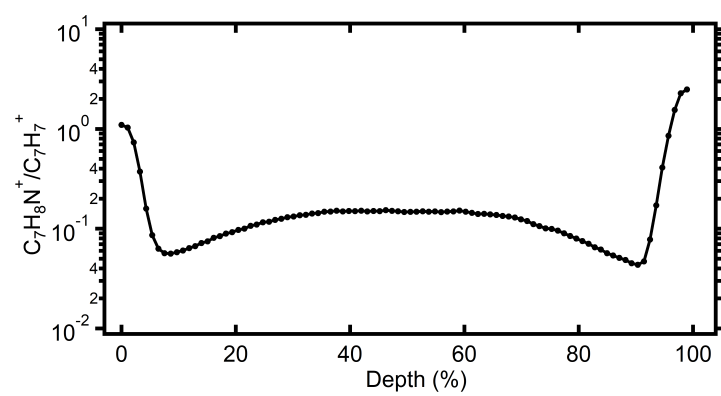


Figure 3.8: $C_7H_8N^+/C_7H_7^+$ signal ratio versus depth (%) plot for P2VP/PS bottlebrush blend with linear PS.

Chapter 4

Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers

The work described in this chapter was done in collaboration with researchers at the Rice University and is submitted for publication:

Charpota, N., Terlier, T., Verduzco, R., Stein, G. E. "Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers".

Nilesh Charpota synthesized and characterized all bottlebrush copolymers, prepared all thin film blends, performed all microscopy measurements, and conducted all surface energy analysis.

4.1 Introduction

The surface composition of polymer blends is usually different from the bulk composition.[69] This attribute, which is controlled by a combination of enthalpic and entropic driving forces, can be leveraged to engineer polymer surfaces with

tailored functions. For example, a simple approach to improve the fouling resistance of commodity polymers is to blend them with an anti-fouling polymer that blooms to the surface during processing.[70–73] Typically, for any film or coating that is processed in air, the surface attraction of a functional polymer additive is controlled by enthalpic preferences at the surface, so these materials are designed with chemistries that reduce their surface energy (γ) relative to the host material.[7, 73–77] This design criterion makes it difficult to develop surface-active functional polymers that increase the polarity (or hydrophilicity) of a polymer surface, as increased polarity is usually correlated with an increase in surface energy.[69]

The design of surface-active functional polymers could also take advantage of entropic effects that arise from differences in the molecular weights or architectures of blend constituents. Numerous theoretical studies and simulations have examined entropy-mediated segregation for the model system of a bidisperse athermal blend,[19, 78–82] and a simple argument that captures the salient physics is that chain ends are preferred over mid-monomers near a surface.[14, 80, 81] Model experiments based on athermal (or nearly-athermal) polymer blends have confirmed that surfaces are usually enriched by the constituent with the highest fraction of chain ends,[14, 15, 68, 83, 84] meaning the constituent with the lowest molecular weight or the highest degree of branching.

A long-standing question in polymer science is to what extent entropic effects can compensate for enthalpic preferences at a surface,[16, 69, 79, 81] leading to a “wetting reversal” where the high energy constituent enriches the surface. A few experimental works have examined this point with miscible, bidisperse blends of linear polymers. In these model cases, the shortest polymer (which has the largest fraction of chain-end monomers) has the highest surface energy. A wetting reversal is achieved when the surface energy gain $\Delta\gamma$ is near-negligible ($\sim 0.2\%$),[17] but is unfavorable as the surface energy gain rises ($\Delta\gamma \sim 4–7\%$).[18, 19] Highly-branched polymers experience a stronger entropic attraction towards surfaces than short-chain linear polymers,[16, 80] so such architectures are promising candidates to expand the range of conditions

for wetting reversal. Indeed, in a miscible blend of a high energy branched polymer and a low energy linear polymer, where $\Delta\gamma$ was approximately 4%,^[19] the high energy branched polymer enriched the free surface.

Bottlebrush polymers are a type of highly-branched polymer architecture. Their synthesis is compatible with a broad range of monomer chemistries,^[21, 85] offering an attractive platform for the design of surface-active polymer additives^[8, 15, 22, 68, 86] with tailored functions.^[8, 23, 73, 87, 88] Our team has studied nearly-athermal blends of bottlebrush and linear polystyrenes, and demonstrated that surface segregation is largely controlled by the relative lengths of linear chains (N_m) and bottlebrush side chains (N_{sc}).^[15, 68] Specifically, when N_m/N_{sc} is greater than approximately 2, the bottlebrush polymer has a larger fraction of chain ends than the linear polymer and enriches the free surface. This simple rule also describes the conditions for surface segregation in thermal blends of bottlebrush and linear polymers, where the surface energy of the bottlebrush is either lower than or similar to that of the linear architecture.^[8, 22, 23]

Here, we leverage the unique architecture and tunable chemistry of bottlebrush copolymers to design high energy, surface-active additives for linear homopolymer hosts. The bottlebrush copolymers are synthesized with a mixture of high energy and “compatibilizing” side chains. We achieve a surface energy gain of $\Delta\gamma = 15\%$, which is the maximum that could be realized for the model chemistries employed in this study. As with athermal blends, the condition of $N_m/N_{sc} > 2$ is necessary for surface enrichment of the bottlebrush copolymer. However, this criterion alone is not sufficient to predict whether the high energy surface is stable through thermal annealing: we find an upper limit on N_m along with a requirement that the bottlebrush have bidisperse side-chain lengths, where the high energy side chains are shorter than the compatibilizing side chains, and we propose that these conditions are necessary to suppress dewetting at the bottlebrush/linear interface. The trends with N_m and N_{sc} should be general, enabling the design of wetting-reversal processes that incorporate chemistries beyond those explored in this work.

4.2 Experimental

4.2.1 Synthesis of Bottlebrush and Linear Polymers

Materials. Linear polystyrene PS₁, PS₂, PS₃ and hydroxy-terminated PS were purchased from Scientific Polymer, Inc. and used as received. Benzene (anhydrous), 4-(Dimethyl amino) pyridine (DMAP) (> 99%), and (CTA) 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (> 98%) a chain transfer agent were used as received from Sigma Aldrich. 2-vinylpyridine (97%) and Styrene (99%) were received from Fisher Scientific and passed through an aluminum oxide column before use. 2-Propanol (99.5%, ACS certified), dichloromethane (DCM) (99.9%, HPLC), diethyl ether (99 %, ACS certified), hexanes (98.5%, ACS certified), aluminum oxide (anhydrous), methanol (99.8%, ACS certified), deuterated chloroform (CDCl₃, 99.8 atom % D) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (98%) were received from Fisher Scientific. Before use 2,2-Azobis(2-methylpropionitrile) (AIBN) was purified by recrystallization in methanol. The third-generation Grubbs ((H₂IMes)(-Pyr)₂(Cl)₂RuCHPh) (G3) catalyst[89] and Bicyclo[2.2.1]hept-5-en-2-ylmethyl 2-(((dodecylsulfanyl)(thioxo)methyl) sulfanyl)-2-methylpropionate (NB-CTA)[90, 91] were synthesized according to previously reported methods.

Exo-5-norbornene-2-carboxylic acid Synthesis (NB-COOH). The synthetic procedure for the synthesis of NB-COOH was adopted from previously reported methods.[90] Norbornene-5-carboxylic acid (endo/exo mixture) (10.00 g, 72.5 mmol) was dissolved in an aqueous solution containing NaHCO₃ (6.700 g, 79.75 mmol, 100 mL of H₂O) in a 1000 mL beaker equipped with a stir bar. In a separate 250 mL beaker, I₂ (12.650 g, 49.5 mmol) and KI (13.239 g, 79.75) were dissolved in 150 mL H₂O. The I₂/KI solution was added dropwise via addition funnel to the 1000 mL beaker containing endo/exo norbornene. The I₂/KI addition was continued until a dark brown color was retained by the solution. The reaction mixture was first filtered

and transferred to a separatory funnel. The solution was washed 3 times with 100 mL diethyl ether to remove iodolactone formed from the endo-norbornene isomer. The aqueous layer was de-colored using a 10 wt% $\text{Na}_2\text{S}_2\text{O}_3$ solution and acidified to $\text{pH} = 2$ by adding 1N H_2SO_4 . The product was extracted by washing the solution 3 times with 100 mL diethyl ether. The organic layer was collected in a separate beaker and dried using MgSO_4 . The product was concentrated by evaporating diethyl ether in a rotary evaporator to obtain a pure product as a white solid.

Conversion of NB-COOH to Norbornene Methanol (NB-MeOH). The synthetic procedure for synthesizing NB-MeOH was adopted from previously reported methods.[90] In a nitrogen-filled glove box, lithium aluminum hydride (0.667 g, 17.570 mmol) was added to a round-bottom flask (100 mL). The round-bottom flask containing lithium aluminum hydride was transferred from the glove box to the fume hood and placed on an ice bath. First, extra dry THF (20 mL) was carefully added drop-wise to the round-bottom flask containing lithium aluminum hydride, followed by a solution of NB-COOH (2.000 g, 16.113 mmol) dissolved in 5 mL extra dry THF. The reaction mixture was allowed to stir on the ice bath for 2-3 minutes. The flask was then removed from the ice bath and placed on an oil bath, already at 75 °C. The round bottom flask was then connected to a reflux condenser, and the reaction was allowed to reflux for 18 hours. After 18 hours, the reaction mixture was removed from the oil bath and placed on an ice bath to cool down. To neutralize lithium aluminum hydride, 1 mL of water was added drop-wise to the reaction mixture which was already stirring on an ice bath, followed by 1 mL of 1N sodium hydroxide and 3 mL of water. The reaction mixture was diluted by adding diethyl ether (200 mL). Finally, solids were removed using gravity filtration, and the filtrate was washed twice in a solution of brine (salt + water). The ether layer was collected, and MgSO_4 was added to remove water. Excess diethyl ether was removed to get a colorless oil.

NB-CTA Synthesis. The synthetic procedure for the synthesis of NB-CTA was adopted from previously reported methods.[91] A 250 mL round-bottom flask was placed on an ice bath, and NB-MeOH (0.860 g, 6.92 mmol), CTA (2.40 g, 6.589 mmol), DMAP (0.161 g, 1.321 mmol) were added. These solid reactants were dissolved in 50 mL extra dry DCM and the reaction mixture was allowed to stir for 5 minutes. In a 20 mL vial, EDC (1.511 g, 7.906 mmol) was dissolved in 2 mL DCM and it was added drop-wise to the reaction mixture, stirring on the ice bath. After adding all the reagents, the round bottom flask was allowed to stir on the ice bath for 10 more minutes. After 10 minutes, the round bottom flask was removed from the ice bath and allowed to stir at room temperature for 24 hours. After 24 hours, the reaction mixture was filtered off, and the crude product was washed once with brine (salt + water) and twice with water. The yellow-colored DCM layer was collected and concentrated by evaporating DCM. Finally, to purify the product column chromatography was performed with 75% DCM and 25% hexanes as mobile phase. The yellow-colored layer was collected, and excess hexanes and DCM were evaporated using a rotary evaporator to obtain a thick yellow oil.

NB-PS Synthesis. Norbornene carboxylic acid (154 mg, 1.114 mmol) was dissolved in 5 mL extra dry DCM in a 25 mL round-bottom flask inside a nitrogen-filled glove box. Oxalyl chloride (0.38 mL, 4.48 mmol) was added to the reaction mixture and the round-bottom flask was sealed with a rubber septum. The sealed round-bottom flask with the reaction mixture was transferred from the glove box to the fume hood. Gas released after mixing oxalyl chloride was let out, and a drop of DMF was added to the flask. The reaction mixture was allowed to react for 10 minutes at room temperature, and the gas released was let out again. After 10 minutes, the reaction was allowed to stir for 4 h at room temperature. After 4 h, excess reagents were removed using a rotary evaporator. Hydroxy-terminated polystyrene (2200 mg, 0.56 mmol) was dissolved in 5 mL extra dry DCM, and the flask was refilled with argon gas. The solution of hydroxy-terminated polystyrene in extra dry DCM was

transferred to the round-bottom flask and the new reaction mixture was sparged with argon for 5 minutes, after which the mixture was stirred for 18 h at room temperature. The polymer was then precipitated in cold methanol. The polymer was isolated by gravity filtration and then redissolved in DCM. The polymer was precipitated again in cold methanol 2 more times to ensure the removal of all impurities. Finally, the product was dried overnight in a vacuum oven for 24 hours.

Synthesis of Bottlebrush Precursor BB-(PS-*co*-CTA) (B_i). Bottlebrush copolymers of NB-PS and NB-CTA were synthesized by ring-opening metathesis polymerization (ROMP) in a nitrogen-filled glove box. In a 20 mL vial equipped with a magnetic stir bar, PS (300 mg, 0.067 mmol, 40 equiv) and NB-CTA (50 mg, 0.1 mmol, 60 equiv) were weighed out and dissolved in 6.9 mL extra dry DCM. In a separate 20 mL vial, a stock solution of G3 with concentration (2.18 mg/mL) was prepared. To initiate the reaction, 0.1 mL of G3 (0.218 mg, 0.000299 mmol, 1 equiv.) solution was transferred to the vial containing the PS and NB-CTA reaction mixture. The reaction was allowed to run for 1 h. After 1 h, the vial containing the reaction mixture was transferred to the fume hood from the glove box. To remove excess G3, the solution was passed through a column of silica gel topped with aluminum oxide. After purification, BB-(PS-*co*-CTA) was obtained by precipitating the reaction mixture in ice-cold methanol. Finally, excess methanol was removed by drying the product under a low vacuum overnight for 24 h.

Synthesis of Bottlebrush Copolymer BB-(PS-*co*-P2VP) (BB_i). Bottlebrush copolymers with a mixture of PS and P2VP side chains were synthesized from the bottlebrush precursor BB-(PS-*co*-CTA) by a grafting-from reaction at 75°C. In a 25 mL round bottom flask equipped with a stir bar, BB-(PS-*co*-CTA) (240 mg, 0.0008 mmol), 2-vinylpyridine (363 mg, 3.45 mmol), CTA (27 mg, 0.073 mmol) and AIBN (1.2 mg, 0.0073 mmol) were added and dissolved in 3.3 mL anhydrous benzene. The round bottom flask was sealed with a rubber septum, and argon was passed through

the reaction mixture for 20 minutes. The flask with the reaction mixture was then placed over an oil bath at 75°C for 18 h. After 18 h, the reaction mixture was allowed to cool down and exposed to oxygen. The reaction mixture was diluted by adding DCM and precipitated in hexanes. The polymer obtained after precipitation was isolated by gravity filtration, redissolved in DCM and precipitated 3 more times to remove impurities. After 3-4 precipitations, the product was dried under low vacuum for 24 h. After drying overnight, free linear P2VP chains were removed by dissolving the product in 2-propanol for 15-20 minutes, and the BB-(PS-*co*-P2VP) was isolated by gravity filtration and dried under low vacuum for 24 h.

Synthesis of Linear P2VP. Linear poly (2-vinylpyridine) was synthesized via RAFT. In a 20 mL round bottom flask, 2-vinylpyridine (2,628 mg, 24.995 mmol), AIBN (11 mg, 0.067 mmol), and CTA (237 mg, 0.649 mmol) were added and dissolved in (2.3 mL) anhydrous benzene. The round bottom flask was sealed with a rubber septum, and argon was passed through the reaction mixture for 20 minutes. The flask with the reaction mixture was placed over an oil bath at 70°C for 18 h. After 18 h, the reaction mixture was allowed to cool down and exposed to oxygen. The reaction mixture was diluted by adding DCM and precipitated in hexanes. The polymer was then isolated by gravity filtration to remove all the impurities. The polymer was redissolved in DCM and precipitated 3 more times and the final polymer was then dried under low vacuum for 24 h.

Safety Statement. No unexpected or unusually high safety hazards were encountered during synthesis of homopolymers or bottlebrush copolymers. Lithium aluminum hydride is a flammable and corrosive powder which must be handled with care. When in contact with water, it releases flammable gases which may ignite spontaneously, and so it is handled inside a nitrogen-purged glove box. The remaining lithium aluminum hydride on spatulas or in vials is deactivated by adding tetrahydrofuran and slowly adding methanol (drop-wise) before discarding. Many of

the organic solvents and monomers used during synthesis are flammable, irritants, and toxic, and must be handled with care inside a fume hood while wearing personal protective equipment (PPE) that includes nitrile gloves, protective clothing, safety glasses, and closed toe shoes.

4.2.2 Characterization

^1H NMR. To obtain ^1H NMR spectra, a 500 MHz Varian spectrometer was used. ^1H shifts were reported in ppm relative to internal solvents. The integrated area from the styrene peak at 6.25-7.3 ppm and norbornene peak at 6.1 ppm was utilized to calculate the average degree of polymerization of NB-PS. Similarly, the integrated area from the CTA peak at 3.25 ppm was compared to the integrated area of the styrene peak at 6.25-7.3 ppm to determine the molar composition of PS and CTA in BB(PS-*co*-CTA). Finally, the integrated area from the CTA peak at 3.25 ppm was compared to the combined integrated areas of styrene and 2-vinylpyridine peaks at 6.25-7.3 and a single peak originating from 2-vinylpyridine peak 7.9-8.4 ppm to determine the molar composition of P2VP and PS in BB(PS-*co*-P2VP). Data were reported in Figures [A.1](#) - [A.13](#).

Gel Permeation Chromatography (GPC). An Agilent 1260 Infinity II GPC instrument with THF as mobile phase operating at 1.0 mL/min flow rate was used to acquire the GPC measurements for linear PS and precursor bottlebrush copolymers. The Agilent GPC instrument was equipped with an Optilab T-rEX RI detector, a ViscoStar III viscometer, and a Wyatt Dawn Helios 8 Multi-Angle Light Scattering Detector. The molecular weights of NB-PS were determined via conventional calibration analysis and universal calibration for BB(PS-*co*-CTA) bottlebrushes. GPC measurements for bottlebrush (PS-*co*-P2VP) were acquired using a PL-GPC 50 Plus system, located at the polymer characterization lab at the University of Tennessee, Knoxville. The system was equipped with a differential refractive index (RI) detector, one PSS GRAL guard column (50 x 8 mm, 10 micron particles,

Polymer Standards Service-USA, Inc.), and two PSS GRAL columns (300 x 8 mm, 10 micron particles, Polymer Standards Service-USA, Inc.). N,N-dimethylformamide (DMF) with 50 mM LiBr was used as the mobile phase, operating at a flow rate of 1.0 mL/min. The measurements were performed at room temperature, and linear polystyrene was used as a standard for calibrating the system. Data were reported in Figures [A.14-A.15](#).

Thin Film Preparation. Thin films were prepared by blending linear PS and bottlebrush copolymers in a (w/w) ratio of 9:1 and dissolving in chlorobenzene, the solution had a 5 wt% total solid concentration. To prepare dry films, clean silicon wafers were obtained after UV treatment, and the solution (linear PS and bottlebrush copolymers in chlorobenzene) was flow coated on the freshly cleaned silicon wafers previously. J.A. Woollam M-2000 spectroscopic ellipsometer was used to characterize the thickness of thin films. The thickness of almost all films ranged between 450-550 nm. To obtain thermally equilibrated films, thermal annealing was carried out for 48 hours at 140 °C inside a nitrogen-filled glove box.

Microscopy. A Nikon LV100 reflected light microscope was used to acquire all the optical microscopy images to detect the roughness on film surfaces. Images were taken at different magnifications, such as 10X, 20X, 50X, and 100X. Atomic force microscopy (AFM) was also performed on films using an Asylum MFP-3D instrument for obtaining height and phase images, tapping mode was used with an image resolution of 256 x 256, scan frequency of 1 Hz and scan size of 5 μm $\times$ 5 μm . First-order flattening was used to process all the images.

Surface Energy. Contact angle measurements were performed using a DataPhysics OCA 15 EC goniometer and at least three of the following probe fluids: diiodomethane, dithioglycol, ethylene glycol, glycerol, and water (Table [A.1](#)). A drop volume of 3 μl was dispensed on the prepared films and imaged for 60 sec at a

rate of 9 frames/sec; three measurements were recorded for each fluid. The contact angle measurements were recorded for 60 s at a rate of 9 frames/s. The liquid contact angle θ was calculated from the drop profiles and plotted on a logarithmic time scale, and the equilibrium value for θ was taken as the average value of the plateau region. The surface energy was calculated by fitting the contact angle data with the Young equation using the model proposed by Owens, Wendt, Rabel and Kaelble (OWRK) [59] to describe the solid-liquid interfacial tension:

$$\frac{\gamma_l \cdot (1 + \cos \theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \quad (4.1)$$

γ_s , γ_{sl} , and γ_l are the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, and the superscripts “p” and “d” designate polar and dispersive components. γ_l^d and γ_l^p are known for each probe fluid. γ_s^d and γ_s^p were determined from Equation 4.1 by nonlinear regression using the curve fit function in SciPy optimize (Python) and are reported with the statistically derived uncertainty. Examples of fitted data are included in Figure A.16.

4.3 Results

Model System. We selected a model system based on a linear PS host and a bottlebrush copolymer additive having a mixture of PS and P2VP side chains, as shown in Figure 4.1. PS and P2VP have similar monomer structures with nearly-identical glass transition temperatures (100 °C), statistical segment lengths, and monomer volumes.[69, 92] However, P2VP is more polar than PS due to the nitrogen heteroatom with a lone electron pair in the aromatic pendant group,[48] and this attribute elevates the surface energy relative to PS by approximately 20% across a broad temperature range.[93, 94] The preference for PS over P2VP at a free surface is well-documented in the literature. For example, in thin films of PS-*b*-P2VP diblock copolymer, the PS block always forms a wetting layer at the free surface.[95, 96]

This phenomenon persists with a P2VP-*b*-PS-*b*-P2VP triblock architecture,[93] even though formation of the PS wetting layer is entropically unfavorable as it depletes the free surface of chain ends.[97] Consequently, if bottlebrush PS-co-P2VP enriches the free surface of a PS film, then the effect is mediated by a strong entropic preference for the bottlebrush architecture at the free surface.

Synthesis. Bottlebrush polymers are often synthesized through the ring-opening metathesis polymerization (ROMP) of norbornenyl-functionalized macromonomers with Grubbs’ third generation (G3) catalyst, a type of “grafting through” reaction.[21, 46, 98] However, ROMP of pyridine-containing macromonomers is not feasible as these moieties strongly interact with the G3 catalyst. This challenge can be addressed by employing a combination of synthetic procedures. [20, 49] As shown in a recent work,[20] bottlebrush block copolymers with pyridine moieties were synthesized by combining “grafting through” and “grafting to” methods: precursors having one block with azide functionalities and another block with densely-grafted PS side chains were synthesized by sequential ROMP. First, norbornene-functionalized polystyrene (NB-PS) macro monomer and NC6Br macro monomer were used to synthesize precursor bottlebrush block copolymers. Azide functionality in NC6Br chains was obtained by nucleophilic substitution of the bromine chain end in the presence of Sodium azide (NaN₃) and Dimethylformamide (DMF). Then alkyne-terminated homopolymers such as P2VP or poly(4-vinylpyridine) (P4VP) were grafted to the azide sites via copper-catalyzed azide-alkyne cycloaddition (CuAAC). For the present work, we devised a hybrid “grafting through” and “grafting from” approach that is illustrated in Figure 4.1: ROMP was used to copolymerize norbornene-functionalized PS (NB-PS) and a norbornene-functionalized chain transfer agent (NB-CTA), and then reversible addition fragmentation chain transfer (RAFT) polymerization was used to synthesize the P2VP side chains. The characteristics of the NB-PS macromonomer, the ROMP products (B₁-B₄), and the final bottlebrush copolymers (BB₁-BB₄) are described in Tables 4.1-4.2. The subscripts on materials in Table 4.2 designate different

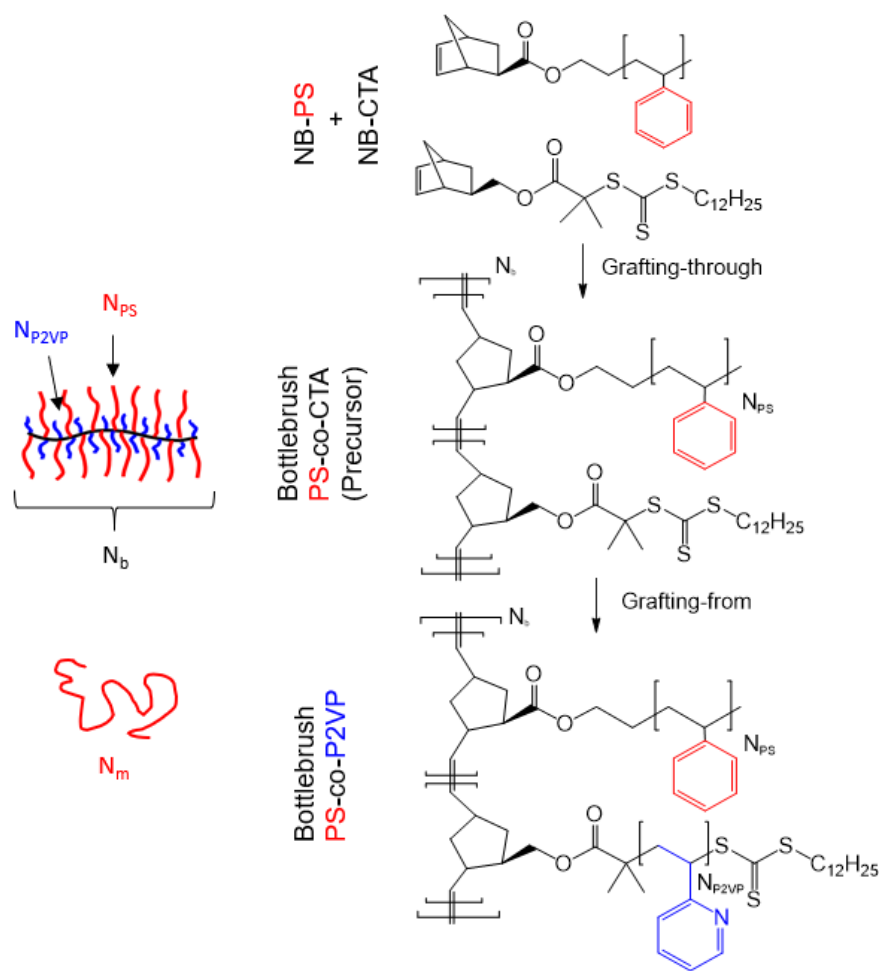


Figure 4.1: (Left) Depiction of bottlebrush PS-*co*-P2VP and linear PS architectures. (Right) Synthesis of bottlebrush PS-*co*-P2VP by a hybrid “grafting-through” and “grafting-from” approach. The molecular fragments colored red and blue are detected in time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of blends.

precursor/product pairs. For example, bottlebrush BB₁ was synthesized from precursor B₁. Characterizations by ¹H NMR and gel permeation chromatography (GPC) are reported in Figures A.1-A.15.

A challenge with the grafting-from polymerization of P2VP side chains is that we cannot reliably determine their molecular weights from GPC analysis of the bottlebrush copolymer. As the GPC analysis consists of a singular peak from BB-(PS-*co*-P2VP), and does not provide any information regarding the molecular weight of side-chains of P2VP present in the bottlebrush copolymer. However, to offer greater control over side-chain dispersity during RAFT, we added 0.2 equivalent of free CTA to the reaction mixture, leading to free P2VP chains in addition to the grafted chains.[99, 100] The molecular weight and dispersity of these free P2VP chains were then characterized by GPC, as shown in Figure A.15, and outcomes are reported in Table 4.2. (Note that free P2VP chains were removed from the bottlebrush copolymer product during the final purification step: BB₁, BB₂, and BB₄ do not have residual free P2VP chains, according to GPC analysis, while BB₃ has approximately 9% impurity.) For comparison, if we assume that all CTA sites on the bottlebrush precursor were activated, then we can estimate the P2VP side chain length from ¹H NMR data of the final purified product. As shown in Table 4.2, the estimates of side-chain length from ¹H NMR are consistent with the GPC analysis of free P2VP chains.

Surface Energies of Bottlebrush Copolymers. Bottlebrush copolymer films with thicknesses in the range of 450-550 nm were prepared by flow coating from chlorobenzene onto clean silicon wafers, followed by thermal annealing at 140 °C for 48 hours in a nitrogen-purged glove box. The surface energy of each bottlebrush copolymer (at room temperature) was determined from measurements of liquid contact angles. The model employed for data analysis describes the total surface energy as the sum of dispersive and polar contributions, i.e., $\gamma_s = \gamma_s^d + \gamma_s^p$. Results are summarized in Figure 4.2a for both as-cast (AC) and thermally-annealed (ANN) films

Table 4.1: Characteristics of PS macromonomer, linear PS, and linear P2VP. M_n is the number-average molecular weight, N_i is the degree of polymerization, $\bar{D}$ is the dispersity.

Polymer	M_n (kg/mol)	N_i	$\bar{D}$
NB-PS	4.5	39	1.05
PS ₁	58	528	1.01
PS ₂	10	96	1.2
PS ₃	20	192	1.01
P2VP _a	10	95	1.15
P2VP _b	4.2	40	1.09

Table 4.2: Characteristics of bottlebrush copolymers. M_w is the weight-average molecular weight; N_b is the average backbone degree of polymerization; $\bar{D}$ is the backbone dispersity; N_{P2VP}^{GPC} is the average degree of polymerization of free P2VP homopolymer from GPC; $\bar{D}_{P2VP}$ is the dispersity of free P2VP homopolymer from GPC; f is either the mol% of NB-CTA in precursor bottlebrush (B₁-B₄) or mol% of 2-vinylpyridine in the final bottlebrush copolymer (BB₁-BB₄); N_{P2VP}^{NMR} is the average degree of polymerization of P2VP side chains from NMR.

Name	Polymer	M_w (kg/mol)	N_b	$\bar{D}$	N_{P2VP}^{GPC}	$\bar{D}_{P2VP}$	f	N_{P2VP}^{NMR}
B ₁	BB-(PS- <i>co</i> -CTA) ₁	209	100	1.4	-	-	60%	-
B ₂	BB-(PS- <i>co</i> -CTA) ₂	370	178	1.24	-	-	60%	-
B ₃	BB-(PS- <i>co</i> -CTA) ₃	215	103	1.27	-	-	60%	-
B ₄	BB-(PS- <i>co</i> -CTA) ₄	320	120	1.2	-	-	50%	-
BB ₁	BB-(PS- <i>co</i> -P2VP) ₁	301	100	1.19	10	1.1	32%	10
BB ₂	BB-(PS- <i>co</i> -P2VP) ₂	431	178	1.28	11	1.2	30%	11
BB ₃	BB-(PS- <i>co</i> -P2VP) ₃	443	103	1.4	36	1.2	60%	30
BB ₄	BB-(PS- <i>co</i> -P2VP) ₄	585	120	1.21	57	1.23	46%	44

along with the standard errors. The surface energies of P2VP and PS homopolymers were measured following the same protocols using films of P2VP_a, PS₁, and PS₃ (Table 4.1).

The calculated surface energies of P2VP and PS homopolymers are 53 mN/m and 42 mN/m, respectively, consistent with literature values,[69] and are unchanged by thermal annealing. The surface energies of both as-cast and thermally-annealed bottlebrush PS-*co*-P2VP are in between the values for P2VP and PS homopolymers at 48 mN/m. This finding demonstrates that a random mixture of PS and P2VP side chains is present at the surface, and the bottlebrush copolymers do not restructure during thermal annealing to enrich the surface with the low-energy PS side chains. The absence of restructuring is attributed to the weak segregation strength χN , where $\chi \approx 0.12$ at 140 °C and $N = N_{PS} + N_{P2VP}$, which ranges from a minimum of approximately 6 for BB₁ and BB₂ up to a maximum of approximately 11 for BB₄. [101, 102] These estimated segregation strengths are either at or below the required threshold for self assembly into distinct PS and P2VP domains ($\chi N_{ODT} \gtrsim 10.5$). [102] Significantly, the surface energy of these bottlebrush copolymers is approximately 15% higher (or 6 mN/m larger) than that of PS at room temperature. While polymer surface energies will decline with increasing temperature, prior studies have shown that the difference in PS and P2VP surface energies remains high at elevated temperatures,[94] so it is reasonable to presume that $\Delta\gamma$ for this bottlebrush PS-*co*-P2VP/linear PS blend remains high at the annealing temperature of 140 °C.

Surface Enrichment in Blends of Bottlebrush Copolymer and Linear Homopolymer. The principal objective of this work is to test whether high energy bottlebrush PS-*co*-P2VP additives can enrich the free surface of a low energy PS film. To examine this point, thin film blends of bottlebrush copolymer (10 wt%) and linear PS were prepared by flow coating from chlorobenzene onto clean silicon wafers, followed by thermal annealing at 140 °C for 48 hours in a nitrogen-purged glove box. The film thicknesses ranged from 450-550 nm. The characteristics of all

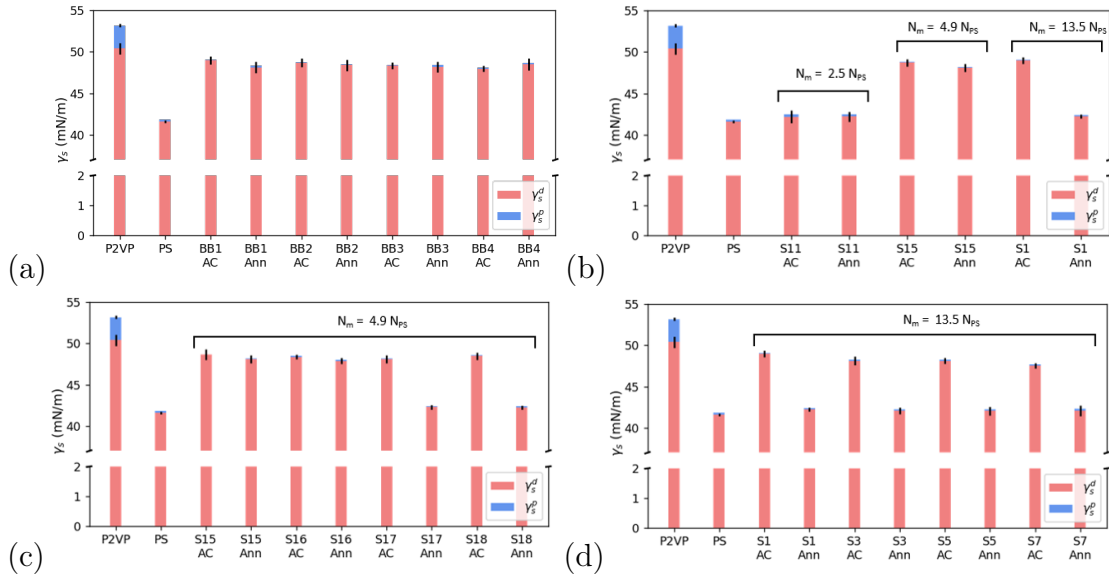


Figure 4.2: Surface energies (γ_s) for as-cast (AC) and thermally annealed (ANN) films of (a) bottlebrush copolymer; (b) blends S11 (BB₁/PS₂), S15 (BB₁/PS₃) and S1 (BB₁/PS₁); (c) blends S15 (BB₁/PS₃), S16 (BB₂/PS₃), S17 (BB₃/PS₃) and S18 (BB₄/PS₃); (d) blends S1 (BB₁/PS₁), S3 (BB₂/PS₁), S5 (BB₃/PS₁), and S7 (BB₄/PS₁). Dispersive (γ_s^d) and polar (γ_s^p) components are represented by red and blue, respectively. Surface energies of P2VP and PS homopolymer are included as references.

Table 4.3: Characteristics of each blend. N_m/N_{PS} is the chain length ratio of PS host to PS side chains, and N_{P2VP}/N_{PS} is the chain length ratio of P2VP and PS side chains.

Blends	Bottlebrush	Linear matrix	N_m/N_{PS}	N_{P2VP}/N_{PS}
S1	BB ₁	PS ₁	13.5	0.26
S3	BB ₂	PS ₁	13.5	0.28
S5	BB ₃	PS ₁	13.5	0.87
S7	BB ₄	PS ₁	13.5	1.3
S11	BB ₁	PS ₂	2.5	0.26
S15	BB ₁	PS ₃	4.9	0.26
S16	BB ₂	PS ₃	4.9	0.28
S17	BB ₃	PS ₃	4.9	0.87
S18	BB ₄	PS ₃	4.9	1.3

blends are summarized in Table 4.3. The through-film composition of these blend films, both as-cast and annealed, was characterized through depth profiling by time-of-flight secondary ion mass spectrometry (TOF-SIMS).[65] This technique probes the surface enrichment of bottlebrush copolymer from changes in the relative $C_7H_8N^+$ to $C_7H_7^+$ signals through a series of analysis/sputter scans, where the $C_7H_8N^+$ fragment is unique to P2VP and the $C_7H_7^+$ fragment is unique to PS (Figure 4.1). The scan number is converted to sputter depth by assuming a constant etch rate. To facilitate comparisons between samples, the film depths are converted to a percent depth, where 0% and 100% designate the free surface and substrate interface, respectively. We note that for all blends of bottlebrush copolymer and PS, irrespective of thermal history or PS molecular weight, TOF-SIMS reveals a strong enrichment of bottlebrush copolymer at the substrate interface (Figures 4.3a-f). This outcome is anticipated: entropic effects favor enrichment of the bottlebrush architecture at a boundary, and P2VP is enthalpically preferred over PS at the native oxide on the clean silicon wafer.[95, 103] The discussion in the following paragraphs is therefore focused on factors that control bottlebrush enrichment at the free surface.

Figures 4.3a-b show TOF-SIMS depth profiles for three blends that all incorporate the BB_1 additive, where the difference between blends is N_m of the PS homopolymer. When N_m is approximately double the length of the PS side chains in the bottlebrush copolymer, as in blend S11 ($N_m/N_{PS}=2.5$), the bottlebrush copolymer is depleted from the free surface of both as-cast and annealed films. When N_m is much larger than N_{PS} , as in blends S15 ($N_m/N_{PS}=4.9$) and S1 ($N_m/N_{PS}=13.5$), the bottlebrush copolymer enriches the free surface of both as-cast and annealed films. These outcomes are consistent with an entropic preference for chain ends at the free surface: The fraction of chain-end monomers in the linear and bottlebrush architectures are $2/N_m$ and approximately $1/N_{PS}$, respectively.[68] Therefore, when $N_m \approx 2N_{PS}$, as in blend S11, linear PS and bottlebrush copolymer have approximately the same fraction of chain-end monomers. As there is no strong entropic preference for either architecture at the surface, the surface is depleted of the high energy bottlebrush

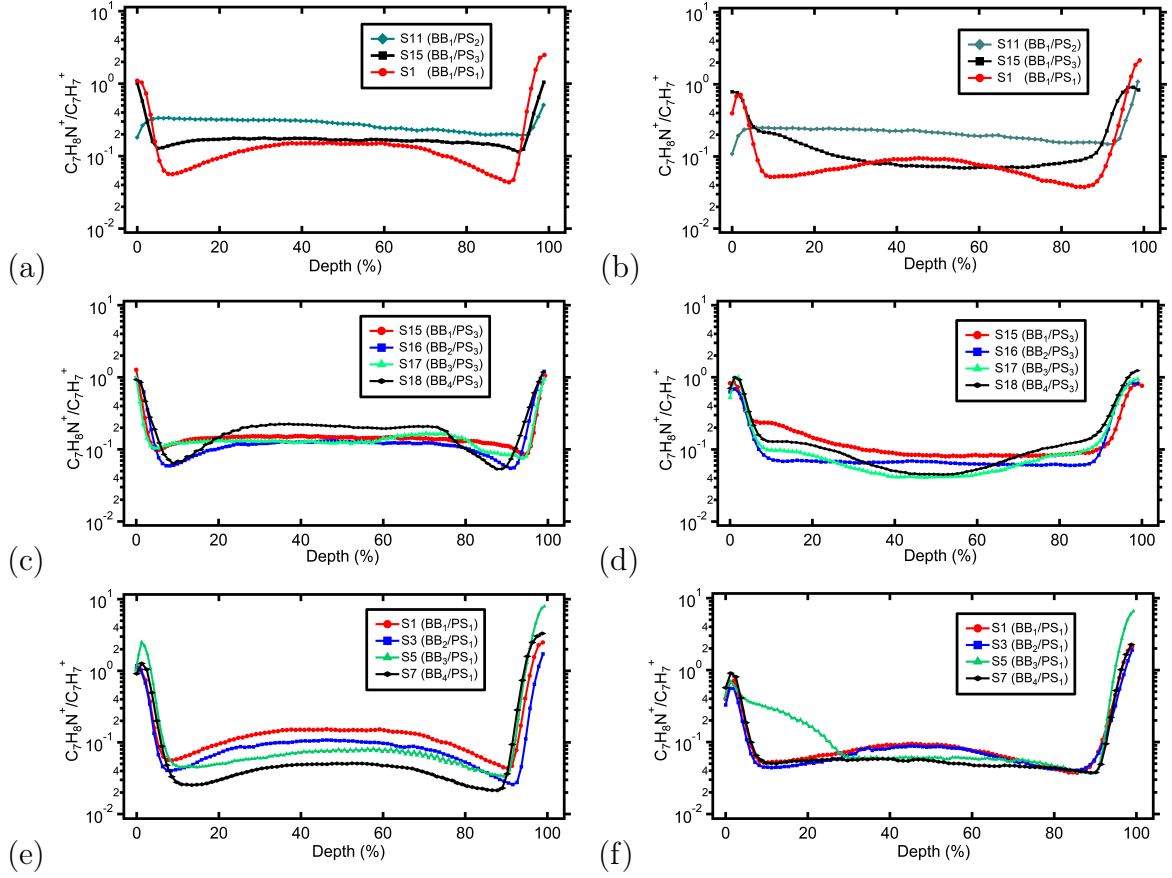


Figure 4.3: TOF-SIMS depth profiles. Top Row: Blends S11 (BB_1/PS_2), S15 (BB_1/PS_3), and S1 (BB_1/PS_1), both as-cast (a) and annealed (b). Middle row: Blends S15 (BB_1/PS_3), S16 (BB_2/PS_3), S17 (BB_3/PS_3), and S18 (BB_4/PS_3), both as-cast (c) and annealed (d). Bottom row: Blends S1 (BB_1/PS_1), S3 (BB_2/PS_1), S5 (BB_3/PS_1), and S7 (BB_4/PS_1), both as-cast (e) and annealed (f).

copolymer. However, when $N_m > 2N_{PS}$, as in blends S15 and S1, the bottlebrush copolymer has a higher fraction of chain ends than the linear PS. Consequently, the bottlebrush is entropically preferred over linear PS at the surface.

The limit where $N_m > 2N_{PS}$ was further studied by preparing blends of each bottlebrush copolymer additive (BB₁-BB₄) with PS₃ ($N_m/N_{PS}=4.9$) and PS₁ ($N_m/N_{PS}=13.5$). For the blends of bottlebrush copolymer with PS₃, which are S15, S16, S17, and S18, the TOF-SIMS depth profiles show enrichment of the bottlebrush copolymer at the free surface in both as-cast and annealed films (Figures 4.3c-d). Similarly, for the blends of bottlebrush copolymer with PS₁, which are S1, S3, S5, and S7 (Figures 4.3e-f), TOF-SIMS depth profiles also show enrichment of the bottlebrush copolymer at the free surface for both as-cast and annealed films. However, we note that blend S5 undergoes an extensive restructuring upon thermal annealing, with a noticeably broadened profile of bottlebrush (or P2VP) enrichment near the free surface.

Surface Energies of Bottlebrush Copolymer/Linear Homopolymer Blends.

Having established the conditions where film surfaces are enriched by bottlebrush copolymer, the surface energy of each blend was measured through contact angle goniometry. Figure 4.2b shows the surface energies for blends of the BB₁ additive with PS homopolymers of varying chain length (S11, S15, and S1), both as-cast and after thermal annealing. The corresponding TOF-SIMS depth profiles for these blends are reported in Figures 4.3a-b. In blends with $N_m/N_{PS} = 2.5$ (S11), where the depth profiles show depletion of the bottlebrush copolymer from the free surface, the surface energies of both as-cast and thermally-annealed films are similar to that of PS homopolymer. In blends with $N_m/N_{PS} = 4.9$ (S15), where the depth profiles show enrichment of bottlebrush copolymer at the free surface, the surface energies of both as-cast and thermally-annealed films are approximately 48 mN/m, which is the same as that of BB₁ (Figure 4.2a). In blends with $N_m/N_{PS} = 13.5$ (S1), where the depth profiles show enrichment of bottlebrush copolymer at the free surface, the

surface energy of as-cast films is approximately 48 mN/m. However, after thermal annealing, the surface energy is reduced to approximately 42 mN/m. While this surface energy measurement appears inconsistent with the TOF-SIMS depth profile, it is important to recognize that the depth profile reports a lateral average of the film composition. Consequently, this technique cannot differentiate between a continuous bottlebrush layer at the surface and a “patchy” surface having domains of bottlebrush embedded within polystyrene. Furthermore, the depth-profiling experiment, which has a depth resolution on the order of 10 nm, cannot reliably detect a thin PS layer at the surface.[65]

Figure 4.2c illustrates the effects of varying the bottlebrush copolymer composition when N_m/N_{PS} is fixed at 4.9 (blends S15, S16, S17, and S18). The corresponding depth profiles show enrichment of bottlebrush copolymer at the free surface in both as-cast and thermally-annealed films (Figures 4.3c-d). The surface energies of as-cast films are similar to that of the bottlebrush copolymers at approximately 48 mN/m. After thermal annealing, the surface energies of blends S15 and S16 remain at 48 mN/m, while the surface energies of blends S17 and S18 are reduced to approximately 42 mN/m. Figure 4.2d illustrates the effects of varying the bottlebrush copolymer composition when N_m/N_{PS} is fixed at 13.5 (blends S1, S3, S5, and S7). The corresponding depth profiles show enrichment of bottlebrush copolymer at the free surface in both as-cast and thermally-annealed films (Figure 4.3e-f). As with the prior series, the surface energies of as-cast films are similar to that of the bottlebrush copolymers at approximately 48 mN/m. However, after thermal annealing, the surface energies of all films are reduced to approximately 42 mN/m. We conclude that for blends where $N_m/N_{PS} > 2$, the surface of as-cast films has a nearly-pure layer of bottlebrush copolymer. However, this nearly-pure bottlebrush copolymer layer remains at the surface only when $N_{P2VP}/N_{PS} \approx 0.25$ and $N_m/N_{PS} = 4.9$ (blends S15 and S16).

Surface Restructuring During Thermal Annealing. The surface energy measurements demonstrate that certain blend surfaces undergo a restructuring during thermal annealing, an effect that is not detected by most of the depth profiling experiments. To better understand how and why the surface restructures, the topography and chemistry of each blend was mapped with optical microscopy (OM), atomic force microscopy (AFM), and TOF-SIMS imaging. The TOF-SIMS image data include a 2D map of the surface as well as a 3D rendering of the through-film composition. We begin by comparing blends S15, S16, S17, and S18, all of which have the same N_m/N_{PS} of 4.9 but incorporate different bottlebrush copolymer additives. Figures 4.4a-b and Figure A.17 show OM, AFM, and TOF-SIMS imaging data for blends S15 (BB₁/PS₃) and S16 (BB₂/PS₃), respectively, which are cases where the high energy surface is stable through thermal annealing. Both the as-cast and annealed surfaces appear smooth in OM and AFM images, and there are no signs of lateral structure in TOF-SIMS images. These data are consistent with both the depth profiles and the surface energy data. For comparison, Figures A.18-A.19 show the same types of imaging data for blends S17 (BB₃/PS₃) and S18 (BB₄/PS₃), which are cases where the surface energy is reduced by thermal annealing. As with blends S15 and S16, the imaging data for both as-cast and annealed films are largely consistent with a smooth, uniform surface, although AFM for blend S18 does show a subtle texture. Therefore, we conclude that an ultrathin (sub-10 nm) layer of PS homopolymer is expelled to the surface of blends S17 and S18 during thermal annealing, as this effect can account for the reduction in surface energy but would be difficult to detect by TOF-SIMS.

We next compare blends S1, S3, S5, and S7, which all have the same N_m/N_{PS} of 13.5 but incorporate different bottlebrush copolymer additives. As-cast films of these blends have a high energy surface, and after thermal annealing, the measured surface energy is reduced towards that of linear PS. Imaging data for blends S1 (BB₁/PS₁) and S3 (BB₂/PS₁) are shown in Figure A.20 and Figure A.21, respectively. Both the as-cast and thermally-annealed films are fairly smooth and uniform. As with blends

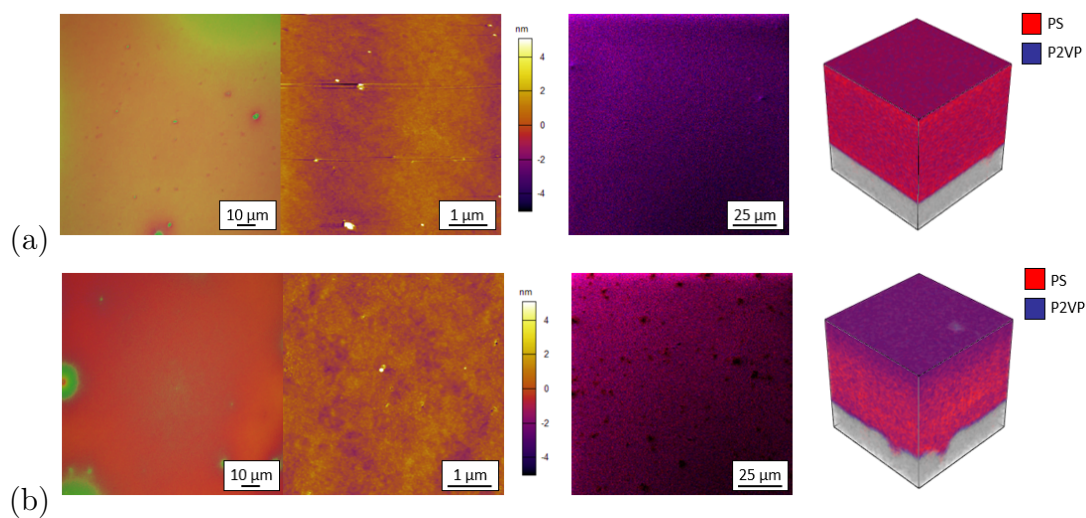


Figure 4.4: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S15 (BB_1/PS_3) (a) as-cast and (b) annealed at 140 °C for 48 hrs.

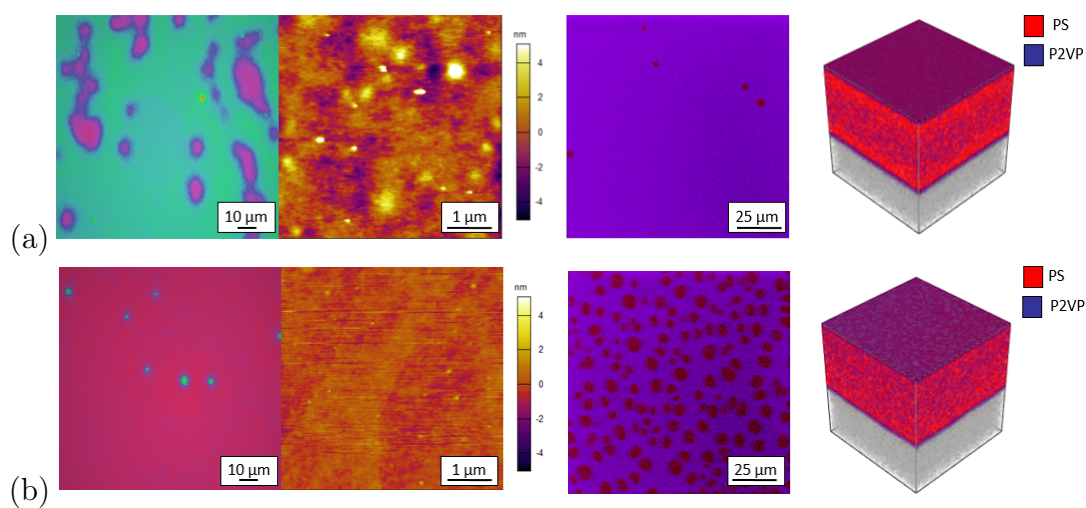


Figure 4.5: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S7 (BB_4/PS_1) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

S17 and S18, we conclude that a thin layer of PS is expelled to the surface of the film during thermal annealing, thereby reducing the surface energy. Imaging data for blends S5 (BB_3/PS_1) and S7 (BB_4/PS_1) are shown in Figure A.22 and Figure 4.5a-b, respectively. As-cast films of both blends have rough surfaces, as revealed by OM and AFM images, and lateral heterogeneities in composition are detected at the surface of blend S5 in TOF-SIMS images. More notably, TOF-SIMS imaging reveals the formation of well-defined microscale domains in the thermally-annealed blends. As the surface energy of these blends is consistent with PS, we conclude that a thin layer of PS is also covering the surface.

4.4 Discussion

The TOF-SIMS data reveal enrichment of the bottlebrush copolymer additives near the surface of both as-cast and thermally-annealed films when N_m/N_{PS} is $\gg 2$, i.e., when the bottlebrush copolymer has a higher fraction of chain ends than the linear PS. This outcome is consistent with our prior studies of athermal blends.[15, 68, 104] Furthermore, the measured surface energies of as-cast films are consistent with that of the high energy bottlebrush copolymers. Notably, to ensure that the high energy surface is stable through thermal annealing, two conditions must be satisfied: First, the linear PS chains should not be “too long” relative to the brush side chains; in this system, “too long” occurs in approximate range of $5 < N_m/N_{\text{sc}} < 14$. Second, the bottlebrush copolymer should have a bidisperse architecture where the P2VP side chains are shorter than the PS side chains ($N_{\text{P2VP}}/N_{\text{PS}} < 1$). These two conditions can be explained by considering the physics that govern dewetting of homopolymers on chemically-identical, surface-attached brushes.[105, 106] Dewetting in such athermal systems is driven by entropy loss of the homopolymer at the brush interface, where the entropy loss rises as the homopolymer chain length increases relative to that of the brush (analogous to increasing N_m/N_{sc}). However, by introducing dispersity in the brush chain lengths (analogous to $N_{\text{P2VP}}/N_{\text{PS}} < 1$), the brush/homopolymer interface

is broadened and the interfacial tension is reduced, thereby suppressing the dewetting process.

The thermodynamics that govern stability of a bottlebrush copolymer/linear PS blend is more complex than that of an athermal, surface-attached brush/homopolymer interface. First, in the bottlebrush-rich surface region, linear PS chains experience a conformational entropy loss from confinement between bottlebrush copolymers. This effect increases with N_m and favors aggregation of the bottlebrush copolymers (which requires expulsion of the linear PS).[107] Second, PS and P2VP are enthalpically incompatible. We anticipate that wetting at a bottlebrush copolymer/linear homopolymer interface will follow the same trends as those established for athermal systems,[108] although the onset of dewetting and bottlebrush-bottlebrush aggregation could shift to lower values of N_m/N_{sc} due to unfavorable enthalpic interactions. However, we postulate that the unfavorable enthalpic interactions between linear PS and the P2VP side chains are partly screened when the P2VP side chains are shorter than the PS side chains, i.e., $N_{P2VP}/N_{PS} < 1$. This statement is supported by our prior studies of bottlebrush polystyrene-co-poly(methyl methacrylate) (PS-co-PMMA) additives in both linear PS and linear PMMA,[22] where PS and PMMA have similar surface energies but are enthalpically incompatible with $\chi \sim 0.03$. [69, 92] The PS side chains in the bottlebrush PS-co-PMMA additives were longer than the PMMA side chains when accounting for differences in monomer volume ($N_{PMMA}/N_{PS} \approx 0.85$). TOF-SIMS revealed enrichment of the bottlebrush PS-co-PMMA in blends with either linear PS or linear PMMA, provided $N_m/N_{sc} > 2$. However, AFM detected microscale domains at the surface of bottlebrush PS-co-PMMA/linear PMMA blends after thermal annealing, while bottlebrush PS-co-PMMA/linear PS blends were smooth and featureless.

With the aforementioned factors in mind, we propose that restructuring of the high energy surface is primarily controlled by dewetting at the bottlebrush copolymer/linear PS interface. As N_m/N_{sc} increases above ca. 2, dewetting leads to expulsion of linear PS from the bottlebrush-rich surface region to the interface

with air. A further increase in N_m/N_{sc} drives separation of the bottlebrush-rich surface region into domains that are enriched by each constituent. However, the use of bottlebrush copolymers with bidisperse side-chain lengths can suppress the onset of dewetting, by both broadening the bottlebrush/linear interface and screening unfavorable enthalpic interactions, thereby stabilizing the high energy surface.

As a final point, we show that a high energy surface cannot be stabilized in a blend of linear P2VP and linear PS. The relevant data are reported in Figures A.23-A.27. In brief, these studies used blends of short-chain linear P2VP_b ($N_{P2VP}=40$) and long-chain PS₁ ($N_m=528$), where the relative fraction of chain ends in P2VP versus PS was $(2/N_{P2VP})/(2/N_m) \approx 13$. The loading of linear P2VP was either 2 wt% or 10 wt%, and according to Flory-Huggins theory with $\chi = 0.12$,^[92] PS₁ and P2VP_b are miscible at both compositions. TOF-SIMS depth profiling reveals enrichment of P2VP at the surfaces of both as-cast blend films, and the surface energy of these films is consistent with that of P2VP. However, after thermal annealing, TOF-SIMS depth profiling reveals enrichment of PS in both blend films, and the surface energy of the films is consistent with that of PS. These control studies confirm that the branched architecture of the bottlebrush copolymer additive is necessary to stabilize a high energy surface through thermal processing.

4.5 Conclusions

We designed surface-active “high energy” bottlebrush copolymer additives that enrich the free surface of a linear commodity homopolymer despite a 15% increase in the surface energy, which is the maximum increase that could be achieved with the chemistries employed in this study. Surface enrichment occurs spontaneously during film casting when the bottlebrush copolymer has a higher fraction of chain-end monomers than the linear homopolymer, reflecting an entropic preference for chain ends over mid-monomers at the film surface. The high energy surface is retained through thermal annealing when dewetting at the bottlebrush copolymer/linear

homopolymer interface is suppressed, which is achieved by employing a bottlebrush with bidisperse side-chain lengths and also limiting the homopolymer chain length relative to that of the bottlebrush side chains, i.e., limiting the ratio N_m/N_{sc} . As this study only probed a narrow parameter space, we expect that further optimization of the bottlebrush architecture could stabilize a high energy surface in blends with larger values of N_m/N_{sc} , which is important for applications that require an entangled polymer matrix. Likewise, expanding the parameter space to include a broader set of chemistries could determine the upper bound on the wetting-reversal process, meaning the maximum gain in surface energy that could be achieved, as a function of polymer chemistry (or χ), additive loading, and the three architectural parameters that characterize the blend system (N_b , N_m , N_{sc}). Significantly, this work provides a foundation to design surface-active additives for polymer films and coatings with substantially relaxed constraints on the choice of additive chemistry, thereby enabling a variety of surface functions that were previously unattainable with a spontaneous segregation process.

Chapter 5

Surface Properties of Thin Films of Bottlebrush Statistical Copolymers

The work described in this chapter has not yet been submitted for publication. Niles Chorpota synthesized and characterized all bottlebrush copolymers and linear copolymers, acquired all SAXS data, and conducted all contact angle measurements and surface energy analysis.

5.1 Introduction

Polymer brushes based on linear statistical copolymers have been used to tailor the wettability and surface energy of an underlying substrate.^[109] However, the synthesis of linear statistical copolymers is limited to monomer pairs that are polymerizable through the same mechanisms. As an example, controlled radical polymerization techniques work well with acrylic and styrenic monomers but cannot be used with olefins or siloxanes. Bottlebrush statistical copolymers can address this limitation while offering potential advantages with manufacturing. As noted in Chapter 2, bottlebrush copolymer synthesis via ROMP (grafting through) can be implemented with nearly any combination of polymer chemistries provided they are soluble in a

mutual solvent. In cases where one chemistry interacts with the ROMP catalyst, the bottlebrush can then be made with a two-step approach. A potential challenge with using bottlebrush statistical copolymers for surface modification is that these systems can undergo self assembly into periodic nanoscale domains.[21, 110] Under conditions that favor self assembly, the domain with the lowest surface energy should form a wetting layer at the free surface.[69] Consequently, the surface properties would resemble the lowest energy side-chain chemistries rather than a mixture of the two (or more) side chain types.

The objective of this research thrust is to establish design rules for tailoring the surface properties of bottlebrush statistical copolymers. We hypothesize that the surface properties of bottlebrush statistical copolymers can mimic those of linear statistical copolymer brushes when the system is in a disordered state, meaning, the bottlebrush copolymer should be weakly segregated and unable to self assemble near a surface. Following the work of Chapter 4, we employ bottlebrush PS-co-P2VP as a model system. A broad set of materials were designed where the number of P2VP side chains and the molar composition of 2-vinylpyridine were independently varied. The bulk structures were measured with small angle X-ray scattering, to test for bulk self assembly, and the surface properties of thin films were evaluated through contact angle goniometry. These studies confirm the hypothesis and also reveal that wettability and surface energy are largely determined by the fraction of P2VP side chains.

5.2 Experimental

5.2.1 Materials

Benzene (anhydrous), chain transfer agent (CTA) 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (> 98%) were used as received from Sigma Aldrich. 2-vinylpyridine (97%, Thermo Scientific) and Styrene (99%, Thermo Scientific)

were received from Fisher Scientific and passed through an aluminum oxide column before use. Dichloromethane (DCM) (99.9%, HPLC), 2-propanol (99.5%, ACS certified), hexanes (98.5%, ACS certified), aluminum oxide (anhydrous) and deuterated chloroform (CDCl_3) (99.8 atom % D) were used as received from Fisher Scientific. 2,2-Azobis(2-methylpropionitrile) (AIBN) was purified by recrystallization in methanol. Mono-hydroxy terminated polystyrene ($M_n = 4,300$ and $10,000$ g/mol) and linear polystyrene ($M_n = 10,000$, $20,000$ and $55,000$ g/mol) were purchased from Scientific Polymers. Other reagents required for synthesizing NB-CTA and bottlebrush copolymers are reported in the experimental section of Chapter 4.

Bottlebrush Copolymer Synthesis and Characterization. The synthetic procedures for the synthesis of NB-COOH, NB-MeOH, NB-CTA, NB-PS39, and BB-(PS39_{0.4}-*co*-CTA_{0.6}) were described in the experimental section of Chapter 4. The synthesis of NB-PS96 followed the same protocol as that for NB-PS39, and the synthesis of BB-(PS39_{0.7}-*co*-CTA_{0.3}) and BB-(PS96_{0.5}-*co*-CTA_{0.5}) followed the same protocol as BB-(PS39_{0.4}-*co*-CTA_{0.6}). The synthesis of BB-(PS39_{0.7}-*co*-P2VP_{0.3}), BB-(PS96_{0.5}-*co*-P2VP_{0.5}), and BB-(PS39_{0.4}-*co*-P2PV_{0.6}) were similar to the protocol in Chapter 4 for synthesis of BB_i bottlebrushes including BB₁-BB₄, except the ratio of 2VP monomer to benzene was changed to 1:1 for the grafting-from reaction.

Linear Copolymer Synthesis and Characterization. A series of linear P(S-*co*-2VP) was synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT). As an example, for synthesis of P(S-*co*-2VP)₂, styrene (2,879 mg, 27.64 mmol), 2-vinylpyridine (2,285 mg, 21.72 mmol), AIBN (2.0 mg, 0.012 mmol) and CTA (15 mg, 0.041 mmol) were added in a round bottom flask with a stir bar and dissolved in 5.2 mL benzene. The reaction mixture was purged in the presence of argon for 10 minutes. After purging, the round bottom flask was placed in an oil bath at 70 °C to initiate the polymerization. After 18 hours, the reaction was quenched by exposing it to oxygen, and the polymer was obtained by precipitation in

hexanes. To remove impurities and unreacted reagents, precipitations were repeated 3 times to get a clean product. The final polymer was dried under low vacuum for 24 hours. ^1H NMR for $\text{P}(\text{S-co-2VP})_1\text{-P}(\text{S-co-2VP})_5$ are shown in Figure B.4 - B.7 and GPC plots are shown in Figure B.23.

5.2.2 ROMP Kinetics.

NB-PS homopolymerization kinetics. Bottlebrush homopolymers of NB-PS were synthesized by ROMP in a nitrogen-filled glove box. Six different reactions were performed using the same amount of initial reagents but a different quenching time. In a 20 mL vial equipped with a magnetic stir bar NB-PS (50 mg, 0.011 mmol, 100 equiv) was dissolved in (0.9 mL) anhydrous DCM. In a separate vial a stock solution of G3 with a concentration of (0.82 mg/mL) was prepared. To start the reactions, 0.1 mL of G3 (0.04 mg, 0.000055 mmol, 1 equiv.) solution in DCM was transferred to NB-CTA. The reactions were allowed to react for 1, 3, 4, 5, 7.5 and 10 min. After the desired time, a few drops of butyl vinyl ether was added to quench the reactions, and cold methanol was used to precipitate the final product. Using gravity filtration, PS bottlebrushes were collected and dried under low vacuum at room temperature to remove excess solvent. NMR spectra were recorded for the NB-PS macromonomer ($t=0$) and the products from each reaction to calculate the conversion. The disappearance of the norbornene peak at 6.1 ppm was monitored after each reaction and compared to the initial norbornene peak in NB-PS macromonomer to get a conversion. Figure B.36-B.42 shows the NMR spectra of reactions after 1, 3, 4, 5, 7.5, and 10 minutes of reaction time.

NB-CTA homopolymerization kinetics. Similarly, bottlebrush homopolymerization of NB-CTA was performed in a nitrogen-filled glove box. Seven different reactions were performed using the same amount of initial reagents but a different quenching time. In a 20 mL vial equipped with a magnetic stir bar NB-CTA (30 mg, 0.064 mmol, 150 equiv), was dissolved in (0.5) mL anhydrous DCM. In a separate

vial, a stock solution of G3 with a concentration of (3.14 mg/mL) was prepared. To start the reactions, 0.1 mL of G3 (0.31 mg, 0.000426 mmol, 1 equiv.) solution in DCM was transferred to NB-CTA. The reactions were allowed to react for 1, 2, 3, 4, 5, 7.5, and 10 min. After the desired time, a few drops of butyl vinyl ether were added to quench the reactions, and the excess solvent from the final product was removed by drying the products under low vacuum at room temperature. NMR spectra were recorded for NB-CTA ($t=0$) and reaction products, and conversion was calculated for each reaction by recording the disappearance of the norbornene peak at 6.1 ppm. Figures B.28- B.35 shows the NMR spectra of NB-CTA bottlebrushes after 1, 2, 3, 4, 5, 7.5, and 10 minutes of reaction time. The disappearance of norbornene peak instantaneously within 1 minute of reaction time implies 100% conversion of NB-CTA to bottlebrush.

Copolymerization kinetics for NB-CTA and NB-PS. Copolymerization kinetics of NB-CTA and NB-PS was performed in a nitrogen-filled glove box. Eight different reactions were performed using the same amount of initial reagents but a different quenching time. In a 20 mL vial equipped with a magnetic stir bar, NB-PS (75 mg, 0.016 mmol, 48 equiv) and NB-CTA (12 mg, 0.025, 72 equiv) were dissolved in (1.6 mL) anhydrous DCM. In a separate vial, a stock solution of G3 with a concentration of (2.25 mg/mL) was prepared. To start the reactions, 0.1 mL of G3 (0.25 mg, 0.000345 mmol, 1 equiv.) solution in DCM was transferred to the reaction mixture. The reactions were allowed to react for 0.5, 1, 2, 3, 4, 5, 7.5 and 10 min. After the desired time, a few drops of butyl vinyl ether were added to quench the reactions and cold methanol was used to precipitate the final product. Using gravity filtration, bottlebrush copolymers were collected and dried under low vacuum at room temperature to remove excess solvent. NMR spectra were recorded for NB-PS macromonomer ($t=0$), and conversion was calculated for each reaction by recording the disappearance of the norbornene peak at 6.1 ppm. Figure B.43-B.50 shows the NMR spectra of NB-CTA and NB-PS bottlebrushes after 0.5, 1, 2, 3, 4, 5, 7.5, and

10 minutes of reaction time. The disappearance of norbornene peak instantaneously within 1 minute of reaction time implies 100% conversion of NB-CTA and NB-PS to bottlebrushes.

Slow down methods. When performing studies of kinetics using G3 catalyst, full conversion was attained within 1 minute. To slow down the reaction, two methods were considered: First, the concentration of G3 was reduced relative to the values employed in typical syntheses. Otherwise, the procedures were the same as detailed above. Second, studies were performed with G1 catalyst, which offers fast initiation but a slower propagation rate than G3.[111] The procedure for performing the kinetic studies with G1 remained the same as described above, but triphenylphosphine was added to further slow down propagation (1 molar equivalent relative to G1).

5.2.3 Characterization

Thin Film Preparation. Thin films were prepared by blending linear PS and bottlebrush copolymers in a (w/w) ratio of 9:1 and dissolving in chlorobenzene, the solution had a 5 wt% total solid concentration. To prepare dry films, clean silicon wafers were obtained after UV treatment, and the solution (linear PS and bottlebrush copolymers in chlorobenzene) was flow coated on the freshly cleaned silicon wafers previously. J.A. Woollam M-2000 spectroscopic ellipsometer was used to characterize the thickness of thin films. Thickness of almost all films ranged between 450-550 nm. To obtain thermally equilibrated films, thermal annealing was carried out for 48 hours at 140 °C inside a nitrogen-filled glove box.

Microscopy. A Nikon LV100 reflected light microscope was used to acquire all the optical microscopy images to detect the roughness on film surfaces. Images were taken at different magnifications, such as 10X, 20X, 50X, and 100X. Atomic force microscopy (AFM) was also performed on films using an Asylum MFP-3D instrument for obtaining height and phase images, tapping mode was used with an

image resolution of 256 x 256, scan frequency of 1 Hz and scan size of 5 μm $\times$ 5 μm . First-order flattening was used to process all the images.

Contact Angle Measurements. Contact angle measurements were performed using a DataPhysics OCA 15 EC goniometer and at least three of the following probe fluids: diiodomethane, dithioglycol, ethylene glycol, glycerol, and water. Water was omitted when calculating the surface energy of any polymer with 2-vinylpyridine at the surface, which includes P(S-co-2VP), linear P2VP, and most bottlebrush PS-co-P2VP, as water can hydrogen bond with pyridine. Hydrogen bonding is not captured in the model employed for polymer/liquid interfacial energy. Ethylene glycol was omitted for films with only PS at the surface at such measurements were always inconsistent with the model, although the reason for this behavior is unclear. A drop volume of 3 μl was dispensed on the prepared films and imaged for 60 sec at a rate of 9 frames/sec; three measurements were recorded for each fluid. The liquid contact angle θ was calculated from the drop profiles and plotted on a logarithmic time scale, and the equilibrium value for θ was taken as the average value of the plateau region.

The surface energy was then calculated by fitting the contact angle data with the Young equation using the model proposed by Owens, Wendt, Rabel and Kaelble (OWRK) [59] to describe the solid-liquid interfacial tension:

$$\frac{\gamma_l \cdot (1 + \cos \theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p} \cdot \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \quad (5.1)$$

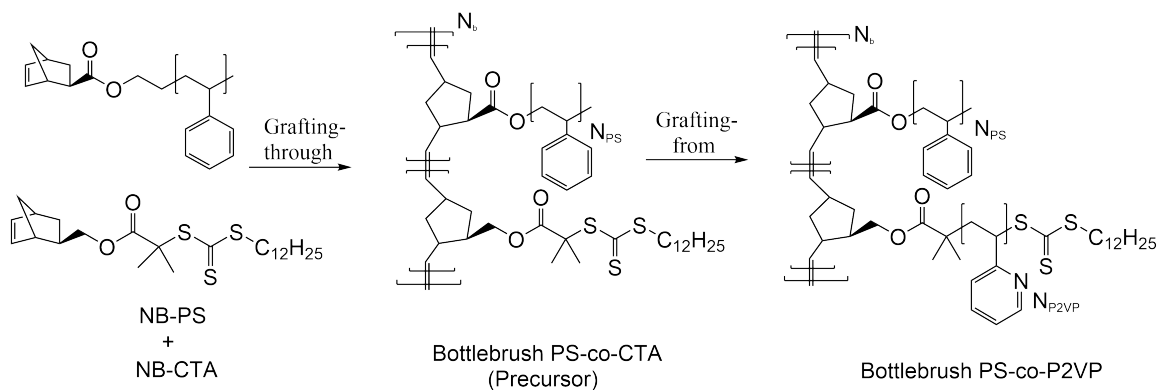
γ_s , γ_{sl} , and γ_l are the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, and the superscripts “p” and “d” designate polar and dispersive components. γ_l^d and γ_l^p are known for each probe fluid. γ_s^d and γ_s^p were determined from Equation 5.1 by nonlinear regression using the curve fit function in SciPy optimize (Python) and are reported with the statistically derived uncertainty. Examples of fitted data are included in Figure B.27.

5.3 Results and Discussion

The bottlebrush PS-co-P2VP materials were synthesized via a hybrid grafting-through and grafting-from approach, as illustrated in Scheme 5.1 and described in Chapter 4 Scheme 4.1. In brief, a norbornene-functionalized chain transfer agent (NB-CTA) was copolymerized with a PS macromonomer (NB-PS) using ring opening metathesis polymerization (ROMP) with the 3rd generation Grubbs (G3) catalyst. P2VP chains were then grown from the bottlebrush PS-co-CTA backbone using RAFT polymerization. Additional “free” CTA was added to the RAFT reaction to improve control over side-chain molecular weights and dispersities,[100, 112] so the crude reaction product was a mixture of bottlebrush PS-co-P2VP and free P2VP chains. The characteristics of the NB-PS macromonomers are reported in Table 5.1, and the characteristics of bottlebrush PS-co-CTA and bottlebrush PS-co-P2VP are summarized in Table 5.2. The materials labeled B₁-B₁₀ are the bottlebrush PS-co-CTA products of the grafting-through reaction, i.e., the precursors to each bottlebrush PS-co-P2VP. The materials labeled BB₁-BB₁₀ are the corresponding bottlebrush PS-co-P2VP products from RAFT polymerization, where compositions were determined after all purification steps. In addition to the shorthand naming of “B_i” and “BB_i”, the materials are also assigned a more descriptive name of BB-(PSX_{1-y}-co-P2VP_y)_i, where “X” is the chain length of the PS macromonomer and “y” is the fraction of chains that are P2VP. The ¹H NMR data and GPC data for all bottlebrush materials are reported in Figures B.8-B.21 and Figures B.22,B.25 and B.26, respectively, aside from materials B₁-B₄ and BB₁-BB₄ which were described in Appendix A.5-A.15. A series of linear P(S-co-2VP) materials were also synthesized by RAFT for comparison with the bottlebrush PS-co-P2VP materials, and their characteristics are reported in Table 5.1.

Table 5.1: Characteristics of NB-PS macromonomers and linear random copolymers of (S) and (2VP). M_n is the number-average molecular weight, N_i is the degree of polymerization, $\mathcal{D}$ is the dispersity, and f is the mol% of 2-vinylpyridine in the copolymer.

Polymer	M_n (kg/mol)	N_i	$\mathcal{D}$	f
NB-PS39	4.5	39	1.05	-
NB-PS96	10	96	1.07	-
P(S-co-2VP) ₀	10	96	1.1	0%
P(S-co-2VP) ₁	20	190	1.12	32%
P(S-co-2VP) ₂	18	171	1.13	50%
P(S-co-2VP) ₃	16	152	1.1	67%
P(S-co-2VP) ₄	17	162	1.08	80%
P(S-co-2VP) ₅	8.5	78	1.15	100%



Scheme 5.1: Synthesis of bottlebrush PS-co-P2VP by a hybrid “grafting-through” and “grafting-from” approach.

Table 5.2: Characteristics of bottlebrush copolymers. M_w is the weight-average molecular weight; N_b is the average backbone degree of polymerization; $\bar{D}$ is the backbone dispersity; N_{P2VP}^{GPC} is the average degree of polymerization of free P2VP homopolymer from GPC; $\bar{D}_{P2VP}$ is the dispersity of free P2VP homopolymer from GPC; f is either the mol fraction of NB-CTA in precursor bottlebrush (B_1 - B_{10}) or mol fraction of 2-vinylpyridine in the final bottlebrush copolymer (BB_1 - BB_{10}); N_{P2VP}^{NMR} is the average degree of polymerization of P2VP side chains from NMR.

Name	Polymer	M_w (kDa)	N_b	$\bar{D}$	N_{P2VP}^{GPC}	$\bar{D}_{P2VP}$	f	N_{P2VP}^{NMR}
B_1	BB-(PS39 _{0.4-co} -CTA _{0.6}) ₁	209	100	1.4	-	-	0.60	-
B_2	BB-(PS39 _{0.4-co} -CTA _{0.6}) ₂	370	178	1.24	-	-	0.60	-
B_3	BB-(PS39 _{0.4-co} -CTA _{0.6}) ₃	215	103	1.27	-	-	0.60	-
B_4	BB-(PS39 _{0.5-co} -CTA _{0.5}) ₄	320	120	1.2	-	-	0.50	-
$^\dagger B_{5,6,7}$	BB-(PS39 _{0.7-co} -CTA _{0.3}) _{5,6,7}	296	89	1.21	-	-	0.30	-
$^\dagger B_{8,9,10}$	BB-(PS96 _{0.5-co} -CTA _{0.5}) _{8,9,10}	485	93	1.35	-	-	0.50	-
BB_1	BB-(PS39 _{0.4-co} -P2VP _{0.6}) ₁	301	100	1.19	10	1.1	0.32	10
BB_2	BB-(PS39 _{0.4-co} -P2VP _{0.6}) ₂	431	178	1.28	11	1.2	0.30	11
BB_3	BB-(PS39 _{0.4-co} -P2VP _{0.6}) ₃	443	103	1.4	36	1.2	0.60	30
BB_4	BB-(PS39 _{0.5-co} -P2VP _{0.5}) ₄	585	120	1.21	57	1.18	0.46	44
BB_5	BB-(PS39 _{0.7-co} -P2VP _{0.3}) ₅	370	89	1.24	29	1.23	0.34	25
BB_6	BB-(PS39 _{0.7-co} -P2VP _{0.3}) ₆	459	89	1.26	72	1.17	0.50	65
BB_7	BB-(PS39 _{0.7-co} -P2VP _{0.3}) ₇	596	89	1.20	91	1.20	0.57	83
BB_8	BB-(PS96 _{0.5-co} -P2VP _{0.5}) ₈	600	93	1.28	36	1.20	0.23	29
BB_9	BB-(PS96 _{0.5-co} -P2VP _{0.5}) ₉	715	93	1.25	78	1.15	0.41	67
BB_{10}	BB-(PS96 _{0.5-co} -P2VP _{0.5}) ₁₀	890	93	1.31	119	1.17	0.56	101

† Note that $B_{5,6,7}$ was the precursor for BB_5 , BB_6 , and BB_7 , while $B_{8,9,10}$ was the precursor for BB_8 , BB_9 , and BB_{10} .

The lengths of the P2VP side chains on the bottlebrushes cannot be directly measured by GPC. Instead, we estimated the P2VP side-chain lengths from GPC analysis of the free P2VP chains ($N_{\text{P2VP}}^{\text{GPC}}$) in the crude RAFT product. These values were close to estimates based on ^1H NMR analysis of the final purified products ($N_{\text{P2VP}}^{\text{NMR}}$) assuming 100% CTA activation: For N near 10, GPC and NMR were in agreement. For N greater than 20, $N_{\text{P2VP}}^{\text{GPC}}$ exceeded $N_{\text{P2VP}}^{\text{NMR}}$ by 10-20 %. Studies have shown that steric effects can suppress the polymerization rate for grafted chains relative to free chains,[113, 114] which could account for the modest discrepancies between GPC and NMR as chain length increased.

The principal objective of this study is to design bottlebrush statistical copolymers that display a mixture of side-chain chemistries at the surface. For this to occur, it is critical to suppress self assembly of the bottlebrush copolymer into distinct PS and P2VP domains: The surface energy of PS is approximately 20% lower than that of P2VP, so the formation of PS domains would lead to PS wetting layers at the surface.[69] Most hydrophobic/hydrophilic polymer pairs have distinct surface energies,[69] so this challenge would also be encountered with other chemistries. Design attributes that control the bulk self assembly of bottlebrush copolymers include the sequence of different side-chain types, the backbone length, the side-chain lengths, and the relative amounts of each type of side chain.[102, 115, 116] If the bottlebrush copolymers have distinct PS and P2VP blocks due to highly non-random incorporation of NB-CTA and NB-PS during ROMP, and if the segregation strength between the PS and P2VP blocks is sufficiently high, then the materials will self-assemble with a domain periodicity that is largely controlled by the backbone length (near 50 nm for BB_1 and BB_3 - BB_{10} , and near 100 nm for BB_2).[46, 117–119] A gradient side-chain sequence rather than distinct blocks will reduce the domain periodicity relative to these estimates.[120, 121] On the other hand, if the bottlebrush copolymers have a random sequence of PS and P2VP side chains, and if the segregation strength between PS and P2VP side chains is sufficiently high, then the

materials will self-assemble with a domain periodicity set by the side chain lengths (near 10 nm for all materials).[46, 119, 122]

As knowledge of the side chain sequence is critical for understanding how the materials might self assemble, and this attribute cannot be measured directly, we attempted measurements of the reactivity ratios for copolymerization of NB-PS and NB-CTA. This approach is based on a terminal model for the copolymerization kinetics,[123] which requires the homopolymerization rate constants as well as the time-resolved concentrations of (macro)monomer and bottlebrush copolymer as inputs. Therefore, we monitored the kinetics of NB-PS39 homopolymerization, NB-CTA homopolymerization, and NB-CTA/NB-PS39 copolymerization. The results are reported in Figure 5.1a-c. The homopolymerization of NB-PS39 is well-described by pseudo first-order kinetics[23, 46, 123, 124] and reached 95% conversion after ten minutes. The homopolymerization rate of NB-PS96 has not yet been measured, but prior studies have found that rates are modestly depressed by increasing the molecular weight of macromonomers.[46] The homopolymerization of NB-CTA reached 100% conversion within 1 minute. These disparate homopolymerization rates reflect both steric effects associated with the relative bulkiness of PS and CTA substituents as well as differences in the anchor group chemistry (see Scheme 5.1).[125, 126] The copolymerization of NB-CTA and NB-PS also reached 100% conversion within 1 minute. As the homopolymerization of NB-CTA and the copolymerization of NB-CTA/NB-PS39 are too fast to monitor the changes in composition with time, these data cannot be used to determine reactivity ratios and predict whether the sequence of NB-PS39 and NB-CTA is random, gradient, or block-like. It is worth noting that other studies have examined the copolymerization of substituted norbornenes by ROMP, and when there are significant differences in the homopolymerization rates of each (macro)monomer, the copolymer tends to have a gradient/blocky sequence.[120, 121, 125]

We attempted to slow down the kinetics for NB-CTA homopolymerization by reducing the G3 catalyst concentration by a factor of 5 while maintaining the same

monomer concentration, but conversion still reached 100% within 1 minute. A further reduction in the catalyst concentration by a factor of 10 led to 93% conversion within 1 minute. Studies that employ even lower catalyst concentrations are underway. Additionally, kinetics were examined using the 1st generation Grubbs catalyst (G1), as G1 produces a slower propagation rate than G3.[111] Triphenylphosphine (PPh3) was added to the reaction to increase the rate of initiation relative to propagation.[127] These data are shown in Figure 5.1d-f. When NB-PS39 was polymerized with G3, the observed rate constant was $k_p = 0.28 \pm 0.02 \text{ min}^{-1}$. When corrected for G3 concentration,[123] the homopolymerization rate is approximately $k_h \approx 2,520 \text{ M}^{-1}\text{min}^{-1}$. When NB-PS39 and NB-CTA were polymerized with G1/PPh3, the observed rate constants were $k_p = 0.020 \pm 0.002 \text{ min}^{-1}$ and $0.165 \pm 0.014 \text{ min}^{-1}$, respectively. When corrected for catalyst concentration, the homopolymerization rates for NB-PS39 and NB-CTA are approximately $k_h \approx 182 \text{ M}^{-1}\text{min}^{-1}$ and $165 \text{ M}^{-1}\text{min}^{-1}$, respectively. As these are similar in magnitude, it seems that G1 does not merely slow down propagation, but interacts with the (macro)monomers in different ways than G3. Alternatively, it is possible that initiation is not fast enough relative to propagation to model the reaction kinetics with the pseudo first-order rate law, so the homopolymerization rates that are extracted from this analysis are incorrect. If efforts to slow down the reaction with G3 are unsuccessful, then future studies will increase the PPh3:G1 ratio to further elevate the initiation rate relative to propagation.[127]

As we were unable to determine reactivity ratios from copolymerization kinetics, we checked for self assembly in each bottlebrush copolymer using small angle X-ray scattering (SAXS). Films with an approximate thickness of 35 μm were prepared by drop-casting from chlorobenzene (5 wt%) onto Kapton. SAXS data were acquired from both as-cast and annealed films (140 $^{\circ}\text{C}$, 48 hrs, nitrogen-purged glove box). The q -range probed in these measurements spanned 0.007 to 1.5 nm^{-1} , so domain periodicities in the range of 90 nm down to 4 nm could be detected. The beam collimation was not optimized for a few measurements, so the low- q data were cutoff

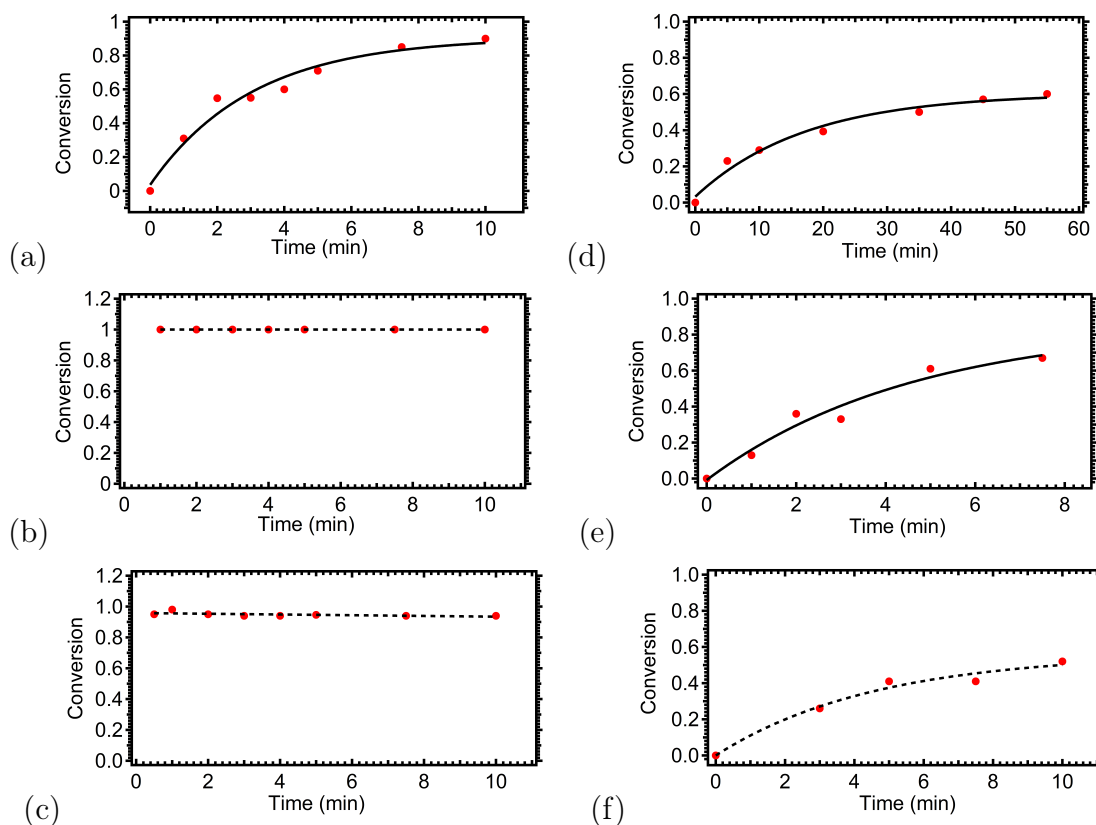


Figure 5.1: ROMP kinetics for (a) NB-PS39 homopolymerization with G3; (b) NB-CTA homopolymerization with G3; (c) copolymerization of NB-PS39 and NB-CTA at a molar ratio of 40:60 with G3; (d) NB-PS39 homopolymerization with G1/PPh3; (e) NB-CTA homopolymerization with G1/PPh3; and (f) copolymerization of NB-PS39 and NB-CTA at a molar ratio of 50:50 with G1/PPh3. Solid lines in parts a, d, and e report the best fit to $\rho = 1 - e^{-k_p t}$. Dashed lines in parts b, c and f are a guide to the eye. All tests used a monomer-to-catalyst molar ratio of 100:1.

at 0.1 nm⁻¹ and the maximum detectable domain periodicity was 63 nm. These q -ranges are sufficiently broad to detect a first-order scattering peak for all bottlebrush copolymers aside from BB₂, as this material has a much longer backbone length and could assemble with a periodicity near 100 nm if possessing distinct blocks of PS and P2VP.

Figure 5.2a shows SAXS data for BB₁-BB₃, materials where 60% of the side chains are P2VP, and Figure 5.2b shows data for BB₅-BB₇, materials where 30% of the side chains are P2VP. The scattering data do not have any signatures of self assembly for either series of materials; all data are identical to the Kapton substrate. However, the absence of structure is useful information when combined with estimates of segregation strength in each potential architecture. The segregation strength χN for a bottlebrush copolymer with distinct PS and P2VP blocks, where $\chi \approx 0.12$ is the Flory interaction parameter at 140 °C and $N \approx N_b(N_{PS} + N_{P2VP})/2$, [102, 115] varies from a minimum of approximately 300 in BB₁ to a maximum of approximately 1000 in BB₁₀. This range might be an overestimate because the value for χ was determined from measurements of linear PS/linear P2VP blends, [101] and therefore does not account for the reduced number of S/2VP contacts in the bottlebrush architecture. [128] Nevertheless, considering the high segregation strengths for a bottlebrush block copolymer relative to that of the order-disorder transition (ODT), where $\chi N_{ODT} \sim 10$, [102, 115, 116] the absence of self-assembled structure means it is highly unlikely that these bottlebrush PS-co-P2VP materials have distinct blocks of each chemistry. The estimated segregation strength χN for an assumed random sequence of side chains, where $N = N_{PS} + N_{P2VP}$, ranges from 6 for BB₁ up to 15 for BB₇. The predicted χN_{ODT} for a bottlebrush random copolymer falls within the approximate range of 10-20, where the value is influenced by the volume fraction of P2VP ($N_{P2VP}/N_{PS}+N_{P2VP}$), the degree of conformational asymmetry (N_{P2VP}/N_{PS}), and the aspect ratio (N_{sc}/N_b). [102] Notably, the estimated χN and predicted χN_{ODT} are similar for a random sequence. The required segregation strength for self assembly in a gradient bottlebrush copolymer is unclear as the degree of non-randomness is

unknown. Consequently, the bottlebrush copolymers could have either a random sequence or a gradient of PS and P2VP side chains, yet be too weakly segregated to undergo self assembly.

Figure 5.2c shows SAXS data for BB₄ and BB₈-BB₁₀, a series of materials where 50% of the side chains are P2VP. There are no signs of self assembly with BB₄. The SAXS signal from BB₈ shows a subtle deviation from the Kapton baseline near $q = 0.2 \text{ nm}^{-1}$. However, samples BB₉ and BB₁₀ produce a scattering peak near $q = 0.18 \text{ nm}^{-1}$, which corresponds to a domain periodicity of 35 nm. As previously discussed, the self-assembled domains arising from a random sequence versus distinct blocks of PS and P2VP side chains would have periodicities near 10 nm and 50 nm, respectively. However, a gradient sequence would produce self assembly at an intermediate length scale. The periodicity of 35 nm is remarkably consistent with that reported for norbornene-based gradient bottlebrush copolymers having backbone lengths of $N_b \sim 100$, similar to the backbone lengths of our materials.[121] Therefore, we conclude that BB₉ and BB₁₀ are gradient copolymers. As BB₈ is made from the same bottlebrush precursor as BB₉ and BB₁₀, that material must also be a gradient copolymer. The difference between these three materials is the P2VP side chain length, which is $N_{\text{P2VP}}^{\text{nmr}} = 29, 67, 101$ for BB₈, BB₉, and BB₁₀, respectively. As seen in Figure 5.2c, the scattering signal increases in intensity as the average side-chain length rises from BB₈ to BB₉ to BB₁₀. This observation is consistent with an increased segregation strength driving self assembly. We note that BB₈, BB₉, and BB₁₀ have the longest average side chain lengths of all the bottlebrush copolymers studied in this work. There are no data available to determine the type of sequence in BB₁-BB₇. The precursors for these materials were derived from copolymerization of NB-CTA and NB-PS39, while the precursor for BB₈, BB₉, and BB₁₀ was derived from copolymerization of NB-CTA and NB-PS96. Considering that the only difference is the molecular weight of the PS macromonomer, we presume that BB₁-BB₇ are also gradient copolymers but self assembly is not observed because the segregation strength is too low.

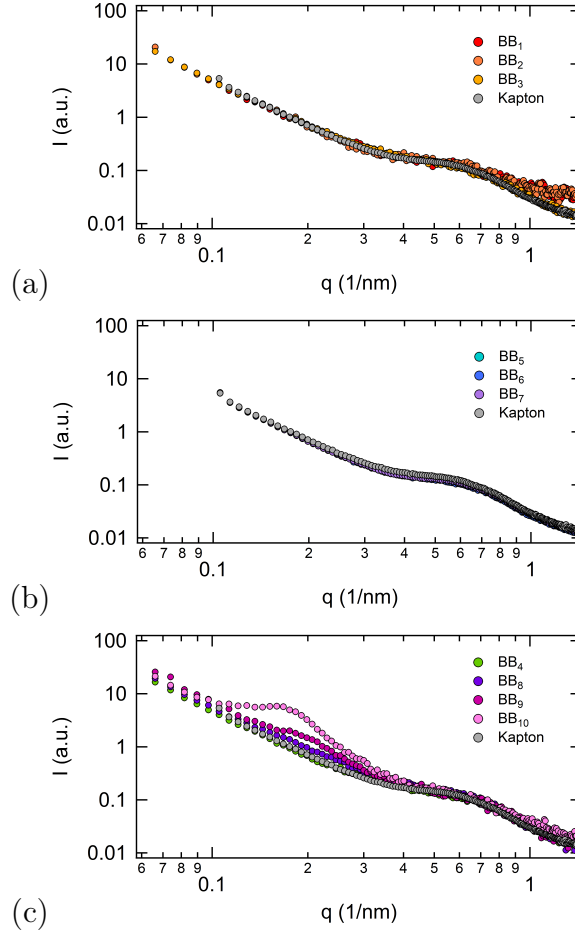


Figure 5.2: SAXS data for annealed films of bottlebrush PS-co-P2VP, grouped by the percentage of side chains that are P2VP. (a) 60% P2VP side chains; (b) 30% P2VP side chains; (c) 50% P2VP side chains. The Kapton substrate is included as a reference.

As bulk samples of BB₉ and BB₁₀ undergo self-assembly into PS and P2VP domains, thin films of these materials will likely have a PS wetting layer at the free surface. The SAXS signal for BB₈ showed a subtle deviation from the Kapton baseline at the same length scale as the self-assembled structures in BB₉ and BB₁₀, so this material might be near the order-disorder transition and could self assemble near a surface. On the other hand, bulk samples of BB₁-BB₇ do not undergo self-assembly, so thin films of these materials should have a mixture of the low-energy PS and high-energy P2VP chains at the surface. To test these hypotheses, the surface energy of all bottlebrush copolymers was estimated from measurements of liquid contact angles. A series of linear P(S-co-2VP) materials, where the composition of 2-vinylpyridine was varied from 0 to 100 mol%, was used as a control. Figure 5.3a-b report the surface energies of all bottlebrush PS-co-P2VP and linear P(S-co-2VP) materials, both as-cast and after thermal annealing. The total surface energy (γ) is reported as a function of the molar composition of 2-vinylpyridine. The surface energy of linear P(S-co-2VP) increases in proportion to 2-vinylpyridine content, from 42 mN/m for 0 mol% P2VP (100 mol% PS) to 53.15 mN/m for 100 mol% P2VP, and is not affected by thermal annealing. The surface energy of bottlebrush PS-co-P2VP is not solely controlled by molar composition of 2-vinylpyridine: Materials BB₁-BB₃, where 60% of the side chains are P2VP, all have a surface energy near 48.5 mN/m even though the composition of 2-vinylpyridine varies from 30-60 mol%. Materials BB₅-BB₇, where 30% of the side chains are P2VP, all have a surface energy near 44 mN/m while the composition of 2-vinylpyridine also varies from 30-60 mol%. Materials BB₄, BB₈, BB₉, and BB₁₀, where 50% of the side chains are P2VP, show more complex behavior: After casting, BB₈ and BB₉ have the same surface energy as linear PS (41.87 mN/m), while BB₁₀ has the same surface energy as the linear P(S-co-2VP) material with 50 mol% 2-vinylpyridine (47.5 mN/m). After thermal annealing, all three bottlebrush copolymers have a surface energy that matches that of linear PS.

The surface energy of the annealed BB₈-BB₁₀ films is consistent with the formation of a PS wetting layer, as expected. It is unclear why as-cast films of BB₈ and BB₉ have

PS wetting layers while as-cast films of BB₁₀ resemble a random copolymer, but a second set of films was prepared to confirm the results were reproducible. Importantly, the surface energies of BB₁-BB₇, both as-cast and annealed, are all consistent with a mixture of PS and P2VP side chains. As shown in Figures 5.3c-d, the surface energies of these bottlebrush copolymers is well-predicted by the fraction of side chains that are P2VP, and these data fall on the same curve as the data for the linear P(S-co-2VP) materials. We postulate that the dependence of bottlebrush surface energy on the fraction of side chains of each type, rather than molar composition, is a consequence of a planar bottlebrush orientation that places a high density of PS and P2VP chain ends at the surface. The liquid droplets do not penetrate very far into this brushy surface layer, and therefore do not sense the average chemistry of the materials.

5.4 Conclusions

Using a model platform of bottlebrush PS-co-P2VP, we demonstrate the design of bottlebrush statistical copolymers with tunable wettability and surface energies. The key to this approach is suppressing the formation of a low-energy PS wetting layer at the film surface. This can be accomplished by designing copolymers that are in a disordered state, meaning they cannot self assemble into distinct domains, by employing short side-chain lengths and a gradient sequence of side-chain types. Interestingly, the surface energy of bottlebrush PS-co-P2VP is controlled by the fraction of P2VP side chains, rather than the molar composition of 2-vinylpyridine, and was nearly identical to that of linear P(S-co-2VP) on this basis. A wide variety of polymer chemistries can be combined in bottlebrush statistical copolymers, as the side chains and backbone are synthesized in independent steps, offering an advantage when compared with linear statistical copolymers.

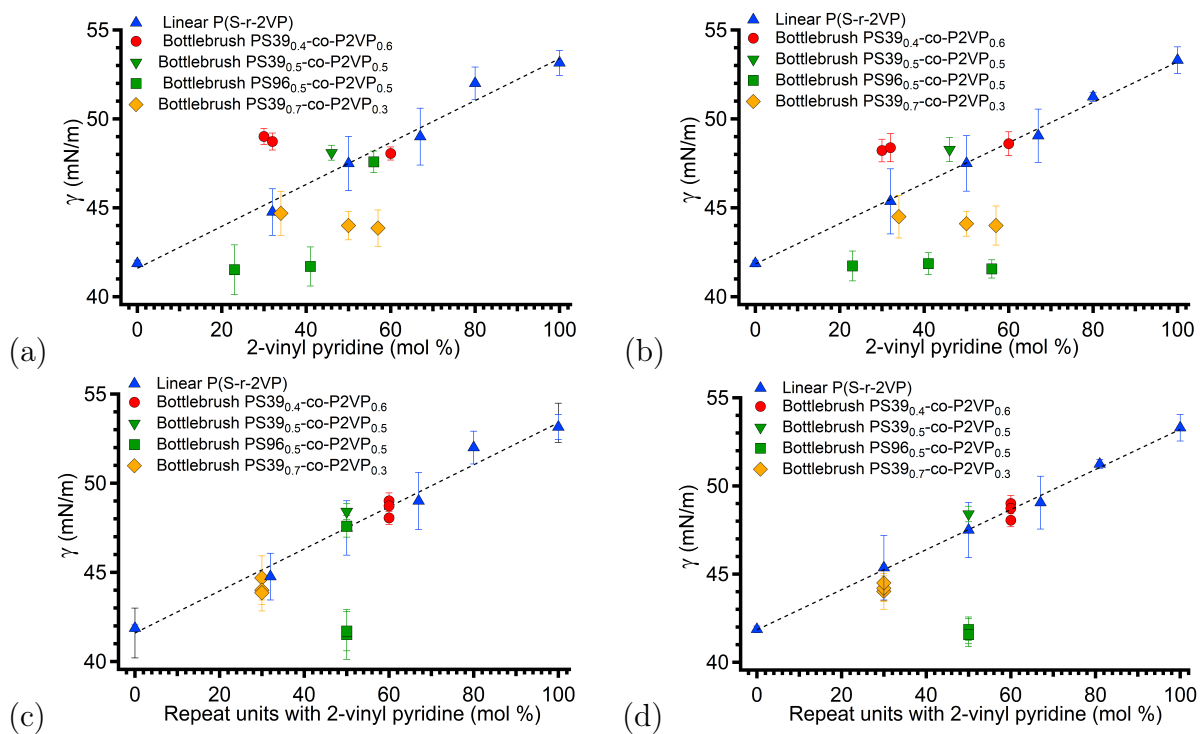


Figure 5.3: Plots for total surface energy vs mole percent of 2-vinylpyridine (a) as-cast (b) annealed at 140 °C for 48 hrs. And plots for total surface energy vs number of repeat units of 2-vinylpyridine (c) as-cast and (d) annealed at 140 °C for 48 hrs.

Chapter 6

Outlook

In Chapter 4, we designed "high energy" bottlebrush copolymer additives that enrich the free surface of linear commodity polymer even after a 15% increase in surface energy. We achieved suppression of dewetting, and high surface energy was retained after thermal annealing when bottlebrush copolymers with bidispersed side chains were employed and the ratio of relative chain lengths of homopolymers to that of side chains of bottlebrush was limited. However, the experiments conducted were probed on a very narrow parameter space, and this process can be optimized in order to stabilize the high-energy surface when the value of N_m/N_{sc} is larger. This can be achieved by various methods. In our current study, the highest surface energy attained for bottlebrush additives was approximately 48 mN/m when the repeat units of P2VP side chains present in the bottlebrushes were 60%. As we know from contact angle measurements, the surface energy of P2VP was approximately 53 mN/m if the repeat units of bottlebrush copolymers were pushed from 60% to (80-90)%, which would certainly increase the surface energy of bottlebrush additives and help us determine the upper-bound of this wetting-reversal process. Another way to push the limit for the wetting reversal process is by expanding the set chemistries that could be used to synthesize these bottlebrush additives. For example, incorporating chemistries with surface energy higher than P2VP. However, incorporating chemistries with very

high surface energy does come with challenges, such as accurately measuring the surface energy of the polymer. As evident from the surface energy measurement of P2VP in Chapter 4, certain polar test fluids, such as water, might not be the best choice for getting static contact angles. Finally, maximum gain in surface energy can be attained, by varying the combination of three main architectural characters of bottlebrush polymers (N_m , N_{sc} and N_b) and additive loading.

As discussed in Chapter 5, a wide variety of side-chain chemistries were required for the study, therefore it was critical that self-assembly of PS and P2VP blocks must be suppressed. From the literature, it has been found that hydrophobic/hydrophilic pairs of polymers have encountered the formation of wetting layers.[69] Design characteristics that control self-assembly in bottlebrush copolymers include the length of the side chain, the length of the backbone, the sequence of side-chain types, and the amount of each side chain. Hence, information regarding the sequence of the side chains is very critical. To calculate the reactivity ratios of NB-CTA and NB-PS for copolymerization, kinetic studies were performed. it was observed that there was a huge discrepancy in rates of homopolymerization as 100% conversion was achieved in homopolymerization of NB-CTA within 1 minute and for the homopolymerization of NB-PS39 95% conversion was reached after 10 minutes. Hence, this method for determining reactivity ratios cannot be used. Another attempt to get the reactivity ratio was attained by decreasing the concentration of G3 used during the homopolymerization of NB-CTA. G3 concentration was decreased by a factor of 5 and 10 but conversion still reached 100% and 93% respectively in 1 minute. Kinetic studies on NB-CTA homopolymerization decreased by a factor of 20 or 30 are required to find the reactivity ratios. Another attempt to examine kinetics using G1 catalyst was performed in the presence of Triphenylphosphine (PPh₃). Results suggested that G1 catalyst interacts with macromonomers much differently than G3 and is not reliable or it is also possible that initiation is not fast enough compared to propagation that kinetics can be modeled in pseudo first-order rate law. Therefore, if efforts to slow down NB-CTA homopolymerization with G3 fail, experiments to

further elevate initiation relative to propagation using G1 catalyst must be performed to get reactivity ratios of NB-CTA and NB-PS for copolymerization.

Bibliography

- (1) Nemani, S. K.; Annavarapu, R. K.; Mohammadian, B.; Raiyan, A.; Heil, J.; Haque, M. A.; Abdelaal, A.; Sojoudi, H. *Advanced Materials Interfaces* **2018**, *5*, 1801247.
- (2) Sojoudi, H.; Nemani, S. K.; Mullin, K. M.; Wilson, M. G.; Aladwani, H.; Lababidi, H.; Gleason, K. K. *ACS applied materials & interfaces* **2019**, *11*, 7330–7337.
- (3) Sojoudi, H.; Arabnejad, H.; Raiyan, A.; Shirazi, S. A.; McKinley, G. H.; Gleason, K. K. *Soft matter* **2018**, *14*, 3443–3454.
- (4) Abu-Isa, I. A. *Journal of Applied Polymer Science* **1971**, *15*, 2865–2876.
- (5) Deng, X.; Korogiannaki, M.; Rastegari, B.; Zhang, J.; Chen, M.; Fu, Q.; Sheardown, H.; Filipe, C. D.; Hoare, T. *ACS Applied Materials & Interfaces* **2016**, *8*, 22064–22073.
- (6) Zhang, H.; Zhao, X.; Wang, X.; Li, Y.; Wang, S. *European Polymer Journal* **2023**, *190*, 112001.
- (7) Schaub, T.; Kellogg, G.; Mayes, A.; Kulasekere, R.; Ankner, J.; Kaiser, H. *Macromolecules* **1996**, *29*, 3982–3990.
- (8) Miyagi, K.; Mei, H.; Terlier, T.; Stein, G. E.; Verduzco, R. *Macromolecules* **2020**, *53*, 6720–6730.
- (9) Kawaguchi, D.; Tanaka, K.; Torikai, N.; Takahara, A.; Kajiyama, T. *Langmuir* **2007**, *23*, 7269–7275.

- (10) Wu, D. T.; Fredrickson, G. H.; Carton, J.-P.; Ajdari, A.; Leibler, L. *Journal of Polymer Science Part B: Polymer Physics* **1995**, *33*, 2373–2389.
- (11) Matsen, M.; Mahmoudi, P. *The European Physical Journal E* **2014**, *37*, 1–8.
- (12) Jones, R. A.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. *Physical review letters* **1989**, *62*, 280.
- (13) Jones, R. A.; Norton, L. J.; Kramer, E. J.; Bates, F. S.; Wiltzius, P. *Physical review letters* **1991**, *66*, 1326.
- (14) Lee, J. S.; Lee, N.-H.; Peri, S.; Foster, M. D.; Majkrzak, C. F.; Hu, R.; Wu, D. T. *Physical Review Letters* **2014**, *113*, 225702.
- (15) Mitra, I.; Li, X.; Pesek, S. L.; Makarenko, B.; Lokitz, B. S.; Uhrig, D.; Ankner, J. F.; Verduzco, R.; Stein, G. E. *Macromolecules* **2014**, *47*, 5269–5276.
- (16) Walton, D.; Mayes, A. *Physical Review E* **1996**, *54*, 2811.
- (17) Hong, P.; Boerio, F.; Smith, S. *Macromolecules* **1994**, *27*, 596–605.
- (18) Kawaguchi, D.; Tanaka, K.; Kajiyama, T.; Takahara, A.; Tasaki, S. *Macromolecules* **2003**, *36*, 6824–6830.
- (19) Walton, D.; Soo, P.; Mayes, A.; Sofia Allgor, S.; Fujii, J.; Griffith, L.; Ankner, J.; Kaiser, H.; Johansson, J.; Smith, G., et al. *Macromolecules* **1997**, *30*, 6947–6956.
- (20) Kim, E. J.; Shin, J. J.; Lee, G. S.; Kim, S.; Park, S.; Park, J.; Choe, Y.; Lee, D.; Choi, J.; Bang, J., et al. *Macromolecules* **2022**, *55*, 1590–1599.
- (21) Verduzco, R.; Li, X.; Pesek, S. L.; Stein, G. E. *Chemical Society Reviews* **2015**, *44*, 2405–2420.
- (22) Mei, H.; Laws, T. S.; Mahalik, J. P.; Li, J.; Mah, A. H.; Terlier, T.; Bonnesen, P.; Uhrig, D.; Kumar, R.; Stein, G. E., et al. *Macromolecules* **2019**, *52*, 8910–8922.

- (23) Laws, T. S.; Mei, H.; Terlier, T.; Verduzco, R.; Stein, G. E. *Langmuir* **2023**, *39*, Publisher: American Chemical Society, 7201–7211.
- (24) Moad, G.; Solomon, D. H., *The chemistry of radical polymerization*, 2nd fully rev. ed, OCLC: 162567493; Elsevier: Amsterdam, 2006.
- (25) *Polymer science: a comprehensive reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier: Amsterdam, 2012, 10 pp.
- (26) Barner-Kowollik, C., *Handbook of RAFT polymerization*, OCLC: 277259412; Wiley-VCH: Weinheim, 2008.
- (27) Gregory, A.; Stenzel, M. H. *Progress in Polymer Science* **2012**, *37*.
- (28) Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T. P.; Boyer, C.; Qiao, G. G. *Chemical reviews* **2016**, *116*, 6743–6836.
- (29) Moad, G. *Polymer International* **2015**, *64*, 15–24.
- (30) Perrier, S. *Macromolecules* **2017**, *50*, 7433–7447.
- (31) Moad, G.; Rizzardo, E.; Thang, S. H. *Chemistry-An Asian Journal* **2013**, *8*.
- (32) Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2012**, *45*, 5321–5342.
- (33) Truett, W.; Johnson, D.; Robinson, I.; Montague, B. *Journal of the American Chemical Society* **1960**, *82*, 2337–2340.
- (34) Calderon, N.; Chen, H. Y.; Scott, K. W. *Tetrahedron Letters* **1967**, *8*, 3327–3329.
- (35) Katz, T. J.; Lee, S. J.; Acton, N. *Tetrahedron Letters* **1976**, *17*, 4247–4250.
- (36) Pesek, S. L.; Li, X.; Hammouda, B.; Hong, K.; Verduzco, R. *Macromolecules* **2013**, *46*, 6998–7005.
- (37) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. *Journal of the American Chemical Society* **2015**, *137*, 1400–1403.

- (38) Bielawski, C. W.; Grubbs, R. H. *Progress in Polymer Science* **2007**, *32*, 1–29.
- (39) *Encyclopedia of polymeric nanomaterials*; Kobayashi, S., Müllen, K., Eds., OCLC: 911384410; Springer Reference: Heidelberg, 2015.
- (40) Bolton, J.; Rzaev, J. *Macromolecules* **2014**, *47*, 2864–2874.
- (41) Cheng, G.; Hua, F.; Melnichenko, Y. B.; Hong, K.; Mays, J. W.; Hammouda, B.; Wignall, G. D. *European polymer journal* **2008**, *44*, 2859–2864.
- (42) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Progress in Polymer Science* **2008**, *33*, 759–785.
- (43) Gao, H.; Matyjaszewski, K. *Journal of the American Chemical Society* **2007**, *129*, 6633–6639.
- (44) Li, Y.; Zou, J.; Das, B. P.; Tsianou, M.; Cheng, C. *Macromolecules* **2012**, *45*, 4623–4629.
- (45) Radzinski, S. C.; Foster, J. C.; Chapleski Jr, R. C.; Troya, D.; Matson, J. B. *Journal of the American Chemical Society* **2016**, *138*, 6998–7004.
- (46) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761–3766.
- (47) Jha, S.; Dutta, S.; Bowden, N. B. *Macromolecules* **2004**, *37*, 4365–4374.
- (48) Kennemur, J. G. *Macromolecules* **2019**, *52*, 1354–1370.
- (49) Zhao, Y.; Zhang, K. *Polym. Chem.* **2016**, *7*, 4081–4089.
- (50) Fürstner, A.; Thiel, O. R.; Lehmann, C. W. *Organometallics* **2002**, *21*, 331–335.
- (51) Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. *Macromolecular rapid communications* **2004**, *25*, 475–480.
- (52) Yuan, Y.; Lee, T. R. In *Surface Science Techniques*, Bracco, G., Holst, B., Eds., Series Title: Springer Series in Surface Sciences; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013; Vol. 51, pp 3–34.
- (53) De Gennes, P.-G. *Reviews of modern physics* **1985**, *57*, 827.

- (54) Annamalai, M.; Gopinadhan, K.; Han, S. A.; Saha, S.; Park, H. J.; Cho, E. B.; Kumar, B.; Patra, A.; Kim, S.-W.; Venkatesan, T. *Nanoscale* **2016**, *8*, 5764–5770.
- (55) Kwak, W.; Park, J. K.; Yoon, J.; Lee, S.; Hwang, W. *Applied Physics Letters* **2018**, *112*.
- (56) Contact Angle Measurement, Theory Relation to Surface Energy, Ossila.
- (57) Fox, H.; Zisman, W. *Journal of Colloid Science* **1952**, *7*, 109–121.
- (58) Fowkes, F. M. *Journal of colloid and interface science* **1968**, *28*, 493–505.
- (59) Owens, D. K.; Wendt, R. *Journal of applied polymer science* **1969**, *13*, 1741–1747.
- (60) Van Oss, C.; Good, R.; Chaudhury, M. *Journal of colloid and Interface Science* **1986**, *111*, 378–390.
- (61) Gindl, M.; Sinn, G.; Gindl, W.; Reiterer, A.; Tschegg, S. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2001**, *181*, 279–287.
- (62) Benninghoven, A. *Angewandte Chemie International Edition in English* **1994**, *33*, 1023–1043.
- (63) Hercules, D. M. *Journal of molecular structure* **1993**, *292*, 49–63.
- (64) *Surface Analysis – The Principal Techniques*, 1st ed.; Vickerman, J. C., Gilmore, I. S., Eds.; Wiley: 2009.
- (65) Mei, H.; Laws, T. S.; Terlier, T.; Verduzco, R.; Stein, G. E. *Journal of Polymer Science* **2022**, *60*, 1174–1198.
- (66) Johansson, B. *Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films* **2006**, *38*, 1401–1412.
- (67) Mahoney, C. M.; Yu, J.; Fahey, A.; Gardella Jr, J. A. *Applied surface science* **2006**, *252*, 6609–6614.

- (68) Mah, A. H.; Laws, T.; Li, W.; Mei, H.; Brown, C. C.; Ievlev, A.; Kumar, R.; Verduzco, R.; Stein, G. E. *Macromolecules* **2019**, *52*, 1526–1535.
- (69) Stein, G. E.; Laws, T. S.; Verduzco, R. *Macromolecules* **2019**, *52*, 4787–4802.
- (70) Hester, J. F.; Banerjee, P.; Mayes, A. M. *Macromolecules* **1999**, *32*, 1643–1650.
- (71) Park, J. Y.; Acar, M. H.; Akthakul, A.; Kuhlman, W.; Mayes, A. M. *Biomaterials* **2006**, *27*, 856–865.
- (72) Gökaltun, A.; Kang, Y. B. (; Yarmush, M. L.; Usta, O. B.; Asatekin, A. *Scientific Reports* **2019**, *9*, 7377.
- (73) Laws, T. S.; Ledford, W. K.; Kurtz, K.; Oyanedel-Craver, V.; Terlier, T.; Tucker, W. C.; Dickenson, N. C.; Ramotowski, T. S.; Kilbey, S. M. I.; Stein, G. E. *ACS Applied Materials & Interfaces* **2023**, *15*, Publisher: American Chemical Society, 28636–28648.
- (74) Chen, X.; Gardella, J. A. J. *Macromolecules* **1994**, *27*, 3363–3369.
- (75) Koberstein, J. T. J.; Duch, D. E. D.; Hu, W.; Lenk, T. J.; Bhatia, R.; Brown, H. R.; Lingelser, J.-P.; Gallot, Y. *The Journal of Adhesion* **1998**, *66*, 229–249.
- (76) Lee, H.; Archer, L. A. *Macromolecules* **2001**, *34*, 4572–4579.
- (77) Koberstein, J. T. *Journal of Polymer Science Part B: Polymer Physics* **2004**, *42*, 2942–2956.
- (78) Yethiraj, A. *Physical Review Letters* **1995**, *74*, 2018–2021.
- (79) Hariharan, A.; Kumar, S. K.; Russell, T. P. *The Journal of Chemical Physics* **1993**, *98*, 4163–4173.
- (80) Wu, D. T.; Fredrickson, G. H. *Macromolecules* **1996**, *29*, 7919–7930.
- (81) Minnikanti, V. S.; Archer, L. A. *Macromolecules* **2006**, *39*, 7718–7728.
- (82) Mahmoudi, P.; Matsen, M. W. *The European Physical Journal E* **2017**, *40*, 85.

- (83) Tanaka, K.; Kajiyama, T.; Takahara, A.; Tasaki, S. *Macromolecules* **2002**, *35*, 4702–4706.
- (84) Hill, J. A.; Endres, K. J.; Mahmoudi, P.; Matsen, M. W.; Wesdemiotis, C.; Foster, M. D. *ACS Macro Letters* **2018**, *7*, 487–492.
- (85) Hyun Kim, K.; Nam, J.; Choi, J.; Seo, M.; Bang, J. *Polymer Chemistry* **2022**, *13*, 2224–2261.
- (86) Mei, H.; Mahalik, J. P.; Lee, D.; Laws, T. S.; Terlier, T.; Stein, G. E.; Kumar, R.; Verduzco, R. *Soft Matter* **2021**, *17*, 9028–9039.
- (87) Pesek, S. L.; Lin, Y.-H.; Mah, H. Z.; Kasper, W.; Chen, B.; Rohde, B. J.; Robertson, M. L.; Stein, G. E.; Verduzco, R. *Polymer* **2016**, *98*, 495–504.
- (88) Kim, K. H.; Kim, M.; Moon, J.; Huh, J.; Bang, J. *ACS Macro Letters* **2021**, *10*, 346–353.
- (89) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, DOI: 10.1021/om010599r, 5314–5318.
- (90) Radzinski, S. C.; Foster, J. C.; Matson, J. B. *Macromolecular rapid communications* **2016**, *37*, DOI: 10.1002/marc.201500672, 616–621.
- (91) Radzinski, S. C.; Foster, J. C.; Chapleski Jr, R. C.; Troya, D.; Matson, J. B. *Journal of the American Chemical Society* **2016**, *138*, DOI: 10.1021/jacs.5b13317, 6998–7004.
- (92) Eitouni, H. B.; Balsara, N. P. In *Physical Properties of Polymers Handbook*, Mark, J. E., Ed.; Springer New York: 2007, pp 339–356.
- (93) Dee, G. T.; Sauer, B. B. *Journal of Colloid and Interface Science* **1992**, *152*, 85–103.
- (94) Sauer, B. B.; Dee, G. T. *Macromolecules* **2002**, *35*, 7024–7030.
- (95) Ji, S.; Liu, C.-C.; Son, J. G.; Gotrik, K.; Craig, G. S. W.; Gopalan, P.; Himpfel, F. J.; Char, K.; Nealey, P. F. *Macromolecules* **2008**, *41*, 9098–9103.

- (96) Stein, G. E.; Kramer, E. J.; Li, X.; Wang, J. *Macromolecules* **2007**, *40*, 2453–2460.
- (97) Matsen, M. W. *Macromolecules* **2010**, *43*, 1671–1674.
- (98) Li, Z.; Zhang, K.; Ma, J.; Cheng, C.; Wooley, K. L. *J. Polym. Sci. A Polym. Chem.* **2009**, *47*, 5557–5563.
- (99) Ohno, K.; Ma, Y.; Huang, Y.; Mori, C.; Yahata, Y.; Tsujii, Y.; Maschmeyer, T.; Moraes, J.; Perrier, S. *Macromolecules* **2011**, *44*, 8944–8953.
- (100) Perrier, S.; Takolpuckdee, P.; Mars, C. A. *Macromolecules* **2005**, *38*, 6770–6774.
- (101) Dai, K. H.; Kramer, E. J. *Polymer* **1994**, *35*, 157–161.
- (102) Chen, D.; Quah, T.; Delaney, K. T.; Fredrickson, G. H. *Macromolecules* **2022**, *55*, 9324–9333.
- (103) Jeu, W. H. d.; Lambooy, P.; Hamley, I. W.; Vaknin, D.; Pedersen, J. S.; Kjaer, K.; Seyger, R.; Hutten, P. v.; Hadziioannou, G. *Journal de Physique II* **1993**, *3*, 8.
- (104) Lee, D.; Charpota, N.; Mei, H.; Terlier, T.; Pietrzak, D.; Stein, G. E.; Verduzco, R. *Macromolecules* **2022**, *55*, 8909–8917.
- (105) Edgecombe, S. R.; Gardiner, J. M.; Matsen, M. W. *Macromolecules* **2002**, *35*, 6475–6477.
- (106) Matsen, M. W.; Gardiner, J. *The Journal of Chemical Physics* **2001**, *115*, 2794–2804.
- (107) Kim, J.; Green, P. F. *Macromolecules* **2010**, *43*, 1524–1529.
- (108) Kim, B.; Ryu, D. Y.; Pryamitsyn, V.; Ganesan, V. *Macromolecules* **2009**, *42*, 7919–7923.
- (109) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* **1997**, *275*, Publisher: American Association for the Advancement of Science, 1458–1460.

- (110) Kim, K. H.; Nam, J.; Choi, J.; Seo, M.; Bang, J. *Polymer Chemistry* **2022**, *13*, Publisher: The Royal Society of Chemistry, 2224–2261.
- (111) Bloch, S. E.; Scannelli, S. J.; Alaboalirat, M.; Matson, J. B. *Macromolecules* **2022**, *55*, Publisher: American Chemical Society, 4200–4227.
- (112) Zhao; Perrier, S. *Macromolecules* **2006**, *39*, 8603–8608.
- (113) Hao, X.; Nilsson, C.; Jesberger, M.; Stenzel, M. H.; Malmström, E.; Davis, T. P.; Östmark, E.; Barner-Kowollik, C. *Journal of Polymer Science Part A: Polymer Chemistry* **2004**, *42*, 5877–5890.
- (114) Duréault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. *Macromolecules* **2004**, *37*, 5513–5519.
- (115) Park, S. J.; Cheong, G. K.; Bates, F. S.; Dorfman, K. D. *Macromolecules* **2021**, *54*, 9063–9070.
- (116) Vigil, D. L.; Quah, T.; Sun, D.; Delaney, K. T.; Fredrickson, G. H. *Macromolecules* **2022**, *55*, 4237–4244.
- (117) Gu, W.; Huh, J.; Hong, S. W.; Sveinbjornsson, B. R.; Park, C.; Grubbs, R. H.; Russell, T. P. *ACS Nano* **2013**, *7*, 2551–2558.
- (118) Dalsin, S. J.; Rions-Maehren, T. G.; Beam, M. D.; Bates, F. S.; Hillmyer, M. A.; Matsen, M. W. *ACS Nano* **2015**, *9*, 12233–12245.
- (119) Levi, A. E.; Lequieu, J.; Horne, J. D.; Bates, M. W.; Ren, J. M.; Delaney, K. T.; Fredrickson, G. H.; Bates, C. M. *Macromolecules* **2019**, *52*, 1794–1802.
- (120) Jiang, L.; Nykypanchuk, D.; Ribbe, A. E.; Rzyayev, J. *ACS Macro Letters* **2018**, *7*, 619–623.
- (121) Jiang, L.; Nykypanchuk, D.; Pastore, V. J.; Rzyayev, J. *Macromolecules* **2019**, *52*, 8217–8226.
- (122) Fei, H.-F.; Yavitt, B. M.; Nuguri, S.; Yu, Y.-G.; Watkins, J. J. *Macromolecules* **2021**, *54*, 10943–10950.

- (123) 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. *Journal of the American Chemical Society* **2017**, *139*, 3896–3903.
- (124) Hyatt, M. G.; Walsh, D. J.; Lord, R. L.; Andino Martinez, J. G.; Guironnet, D. *J. Am. Chem. Soc.* **2019**, *141*, 17918–17925.
- (125) Chang, A. B.; Lin, T.-P.; Thompson, N. B.; Luo, S.-X. L.; Liberman-Martin, A. L.; Chen, H.-Y.; Lee, B.; Grubbs, R. H. *Journal of the American Chemical Society* **2017**, *139*, 17683–17693.
- (126) Radzinski, S. C.; Foster, J. C.; Chapleski, R. C.; Troya, D.; Matson, J. B. *Journal of the American Chemical Society* **2016**, *138*, 6998–7004.
- (127) Bielawski, C. W.; Grubbs, R. H. *Macromolecules* **2001**, *34*, Publisher: American Chemical Society, 8838–8840.
- (128) Zhang, B.; Cui, S.; Lodge, T. P.; Bates, F. S. *Macromolecules* **2023**, *56*, 1663–1673.

Appendix

Appendix A

Supporting Characterization for: Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers.

A.1 ^1H NMR

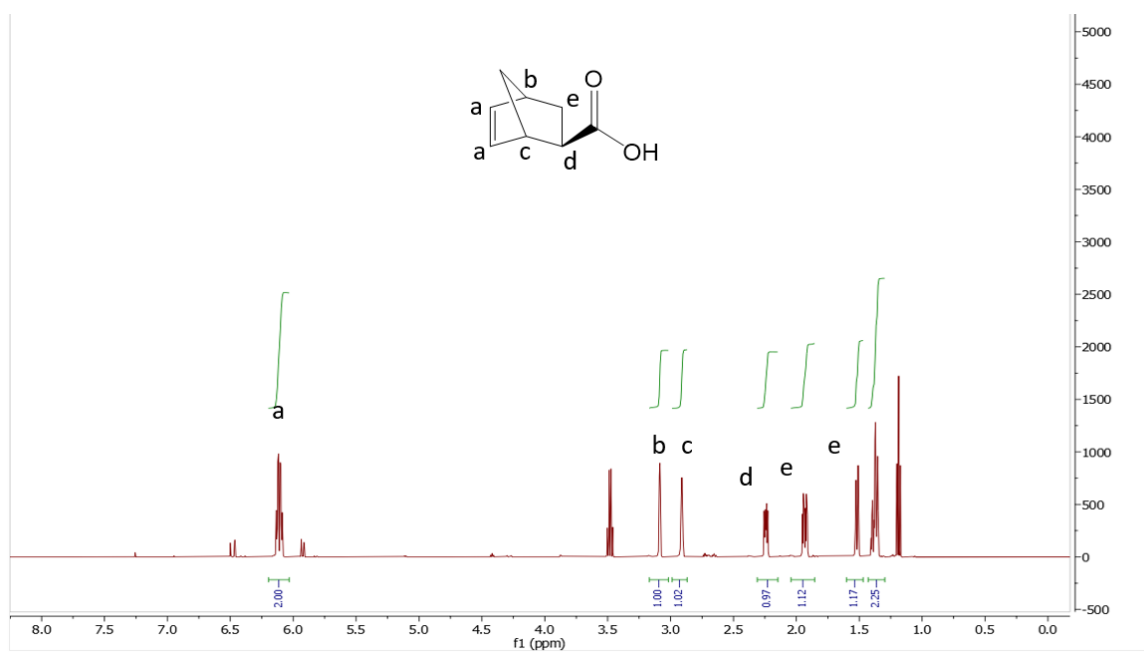


Figure A.1: NMR spectrum for exo-5-norbornene-2-carboxylic acid.

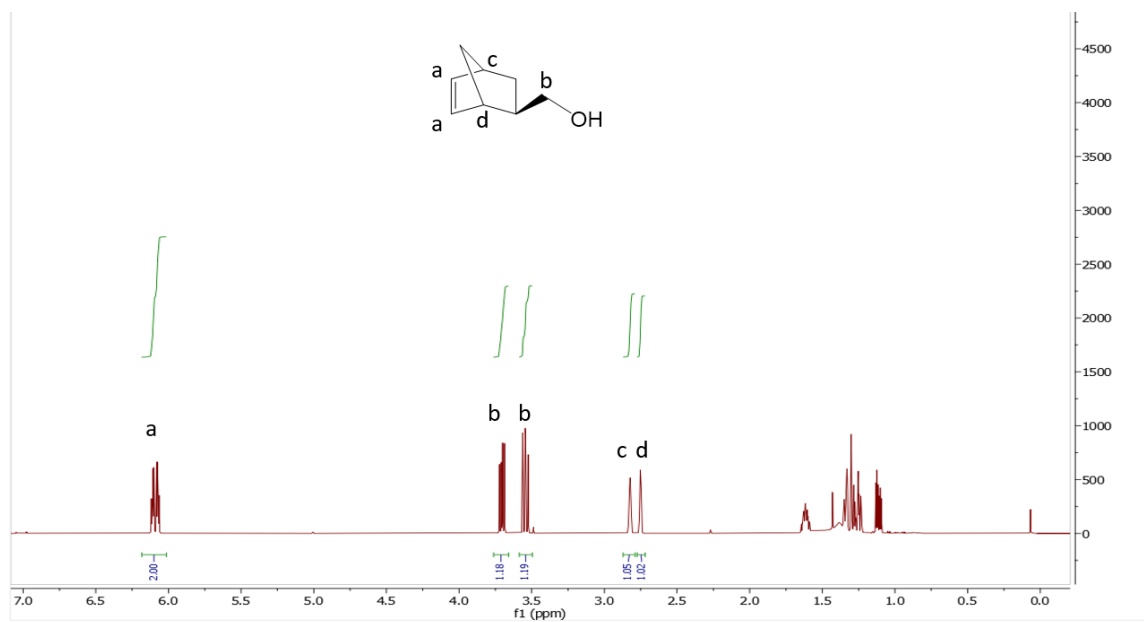


Figure A.2: NMR spectrum for norbornene methanol (NB-MeOH).

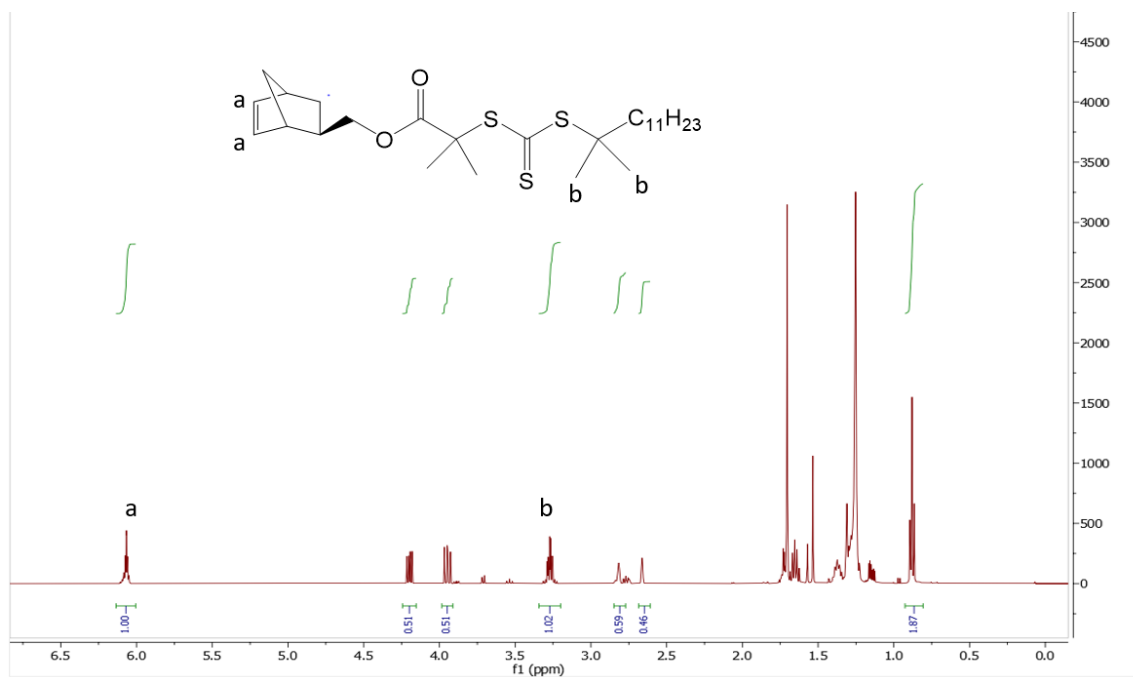


Figure A.3: NMR spectrum for NB-CTA. The appearance of the CTA peak (b, 2H, 3.25 ppm) confirms a successful coupling reaction.

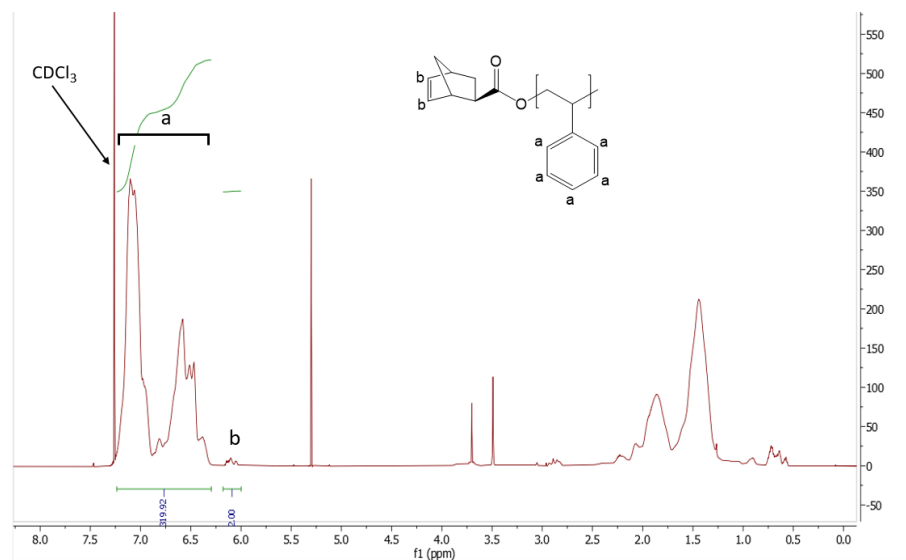


Figure A.4: NMR spectrum for NB-PS. The protons from styrene (a, 5H, 6.25-7.3 ppm) were integrated relative to the protons from norbornene (b, 2H, 6.1 ppm) to obtain the average degree of polymerization of the polymer.

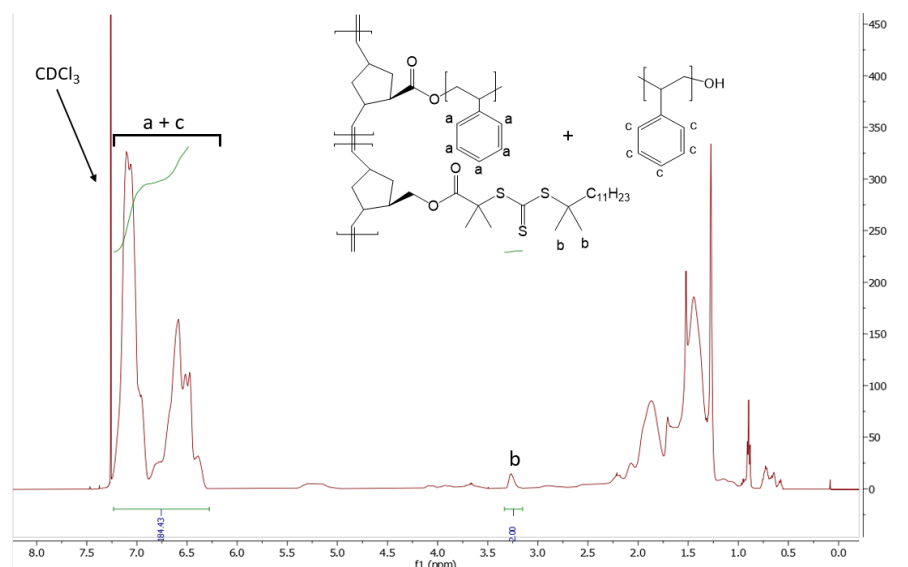


Figure A.5: NMR spectrum for B₁ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm) and (c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. The styrene peak contains PS from precursor bottlebrush and unincorporated PS. The relative amounts were determined from GPC.

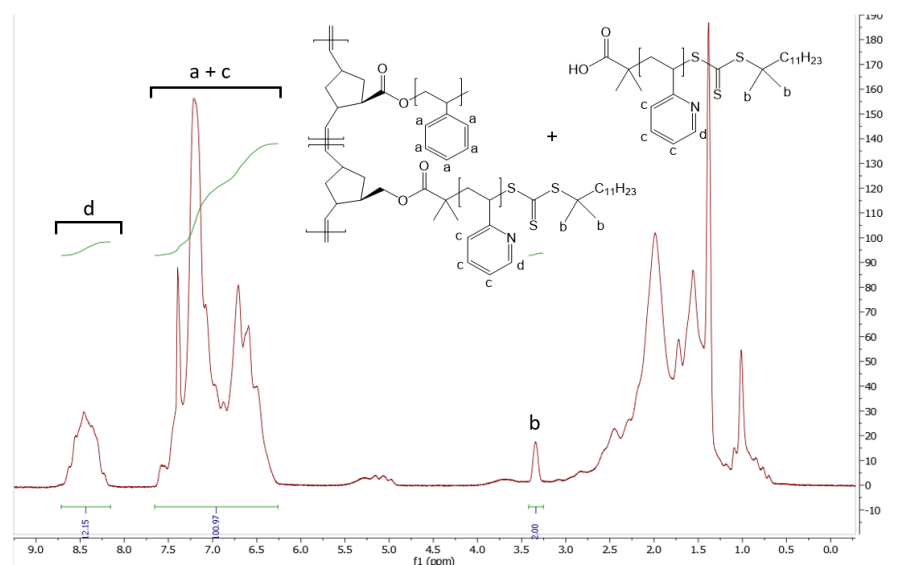


Figure A.6: NMR spectrum for BB₁ and linear P2VP. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 ppm; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain the mole percent of each polymer.

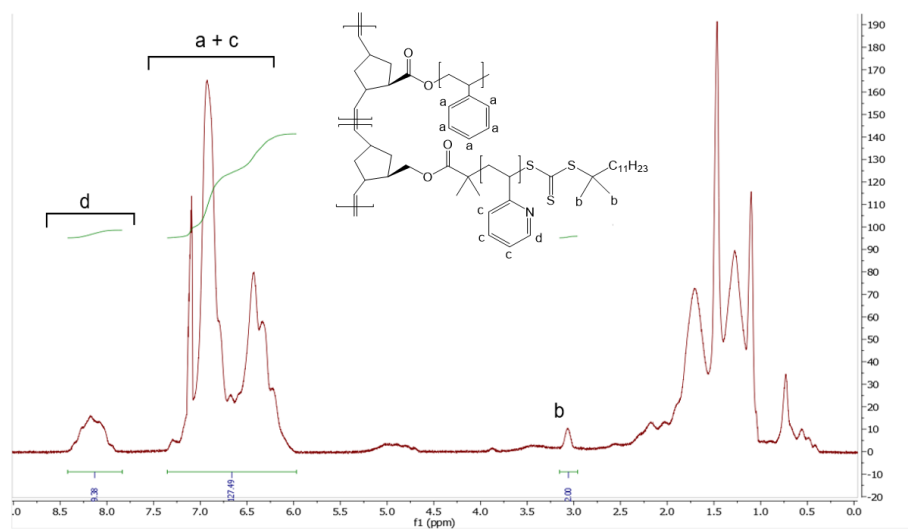


Figure A.7: NMR spectrum for BB₁. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

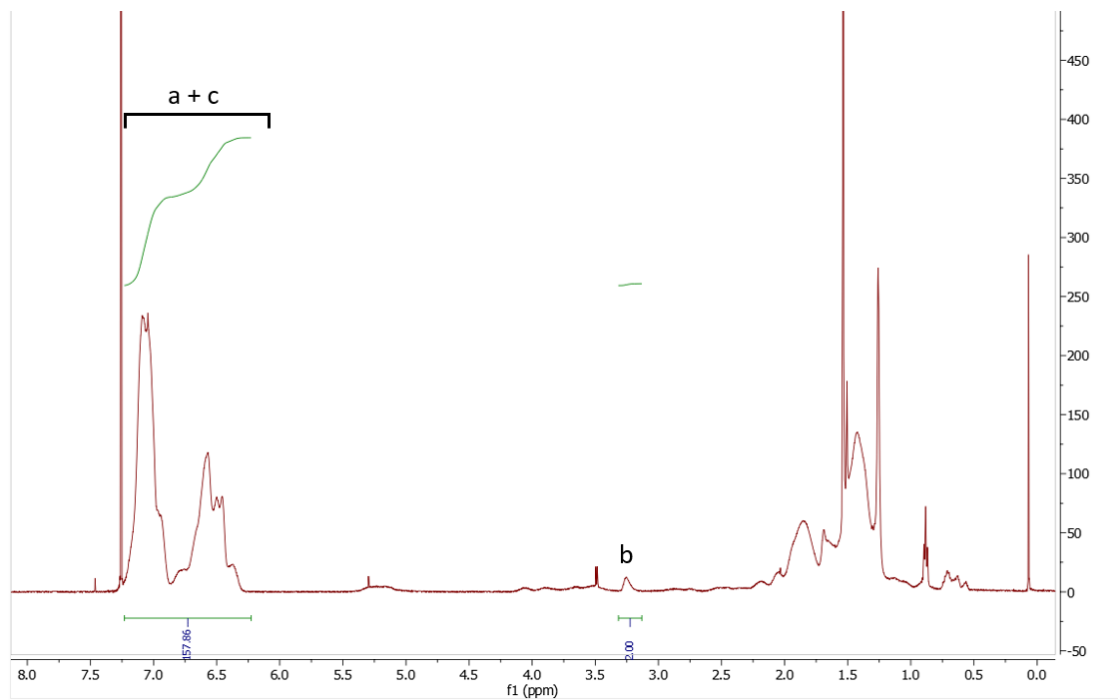


Figure A.8: NMR spectrum for B₂ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.

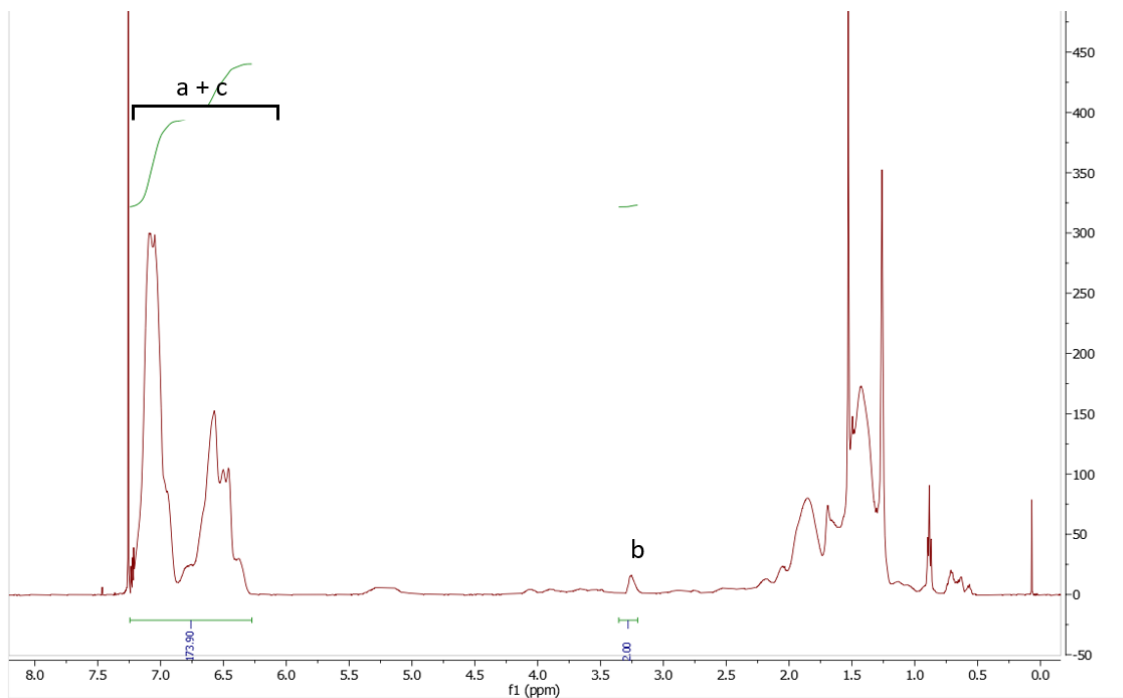


Figure A.9: NMR spectrum for B₃ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.

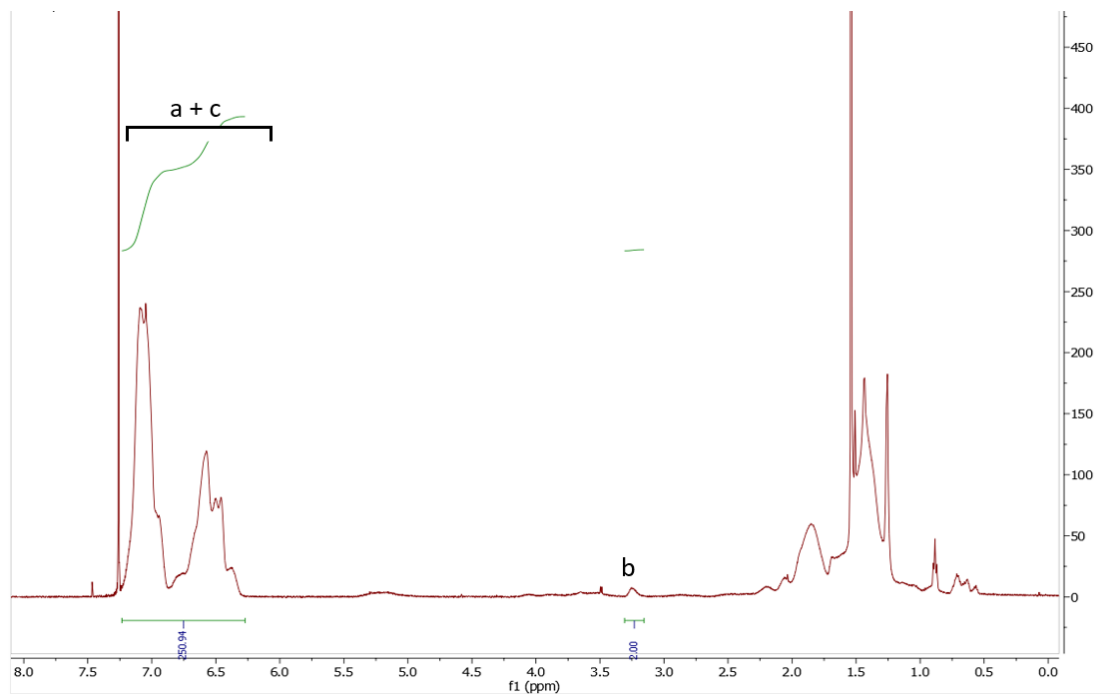


Figure A.10: NMR spectrum for B₄ with unincorporated PS-OH. The protons from styrene (a, 5H, 6.25-7.3 ppm and c, 5H, 6.25-7.3 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain mole percent of PS as compared to NB-CTA. See Figure A.5 for bottlebrush copolymers and unincorporated PS-OH structures.

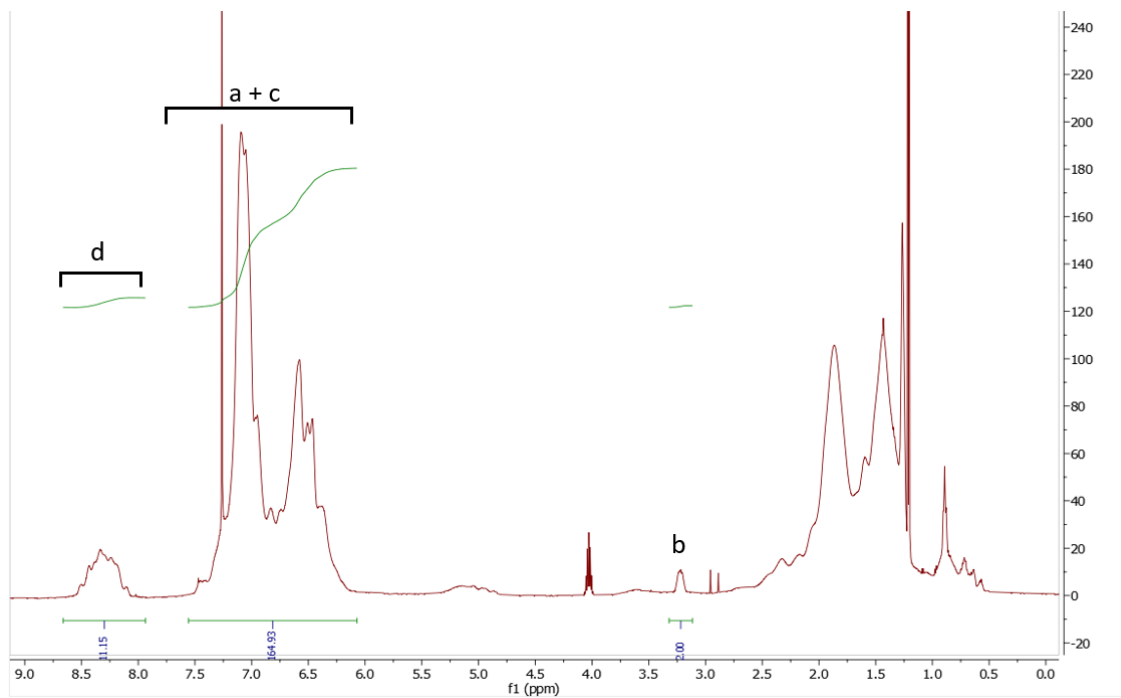


Figure A.11: NMR spectrum for BB₂. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB₂ structure.

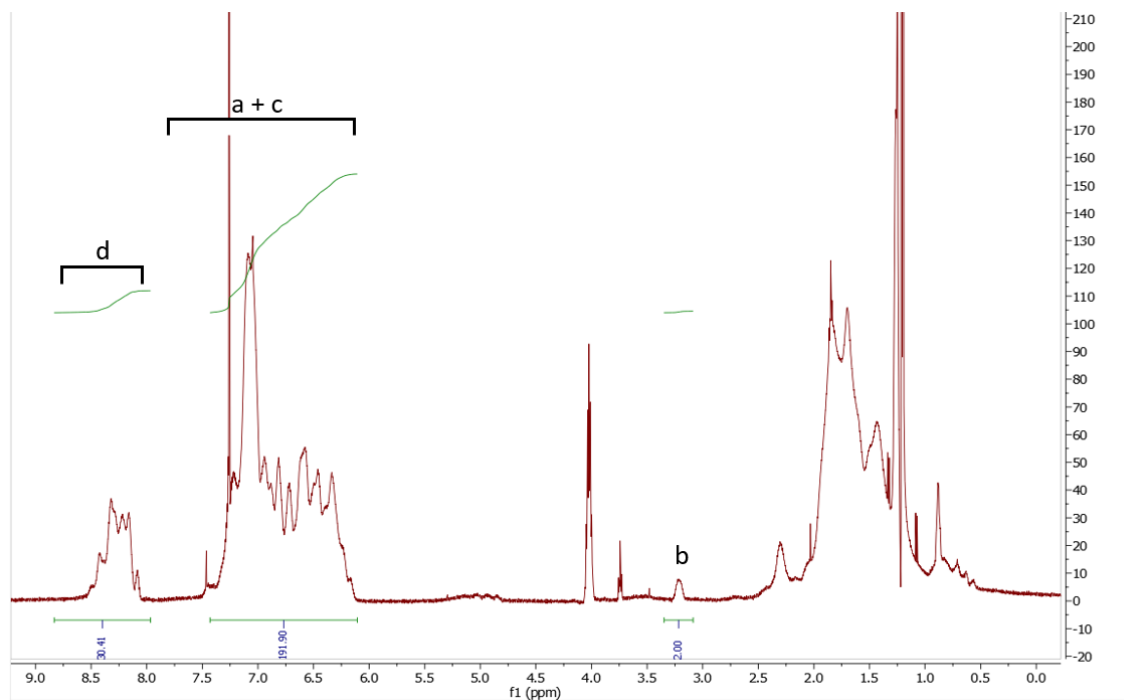


Figure A.12: NMR spectrum for BB₃. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB₃ structure.

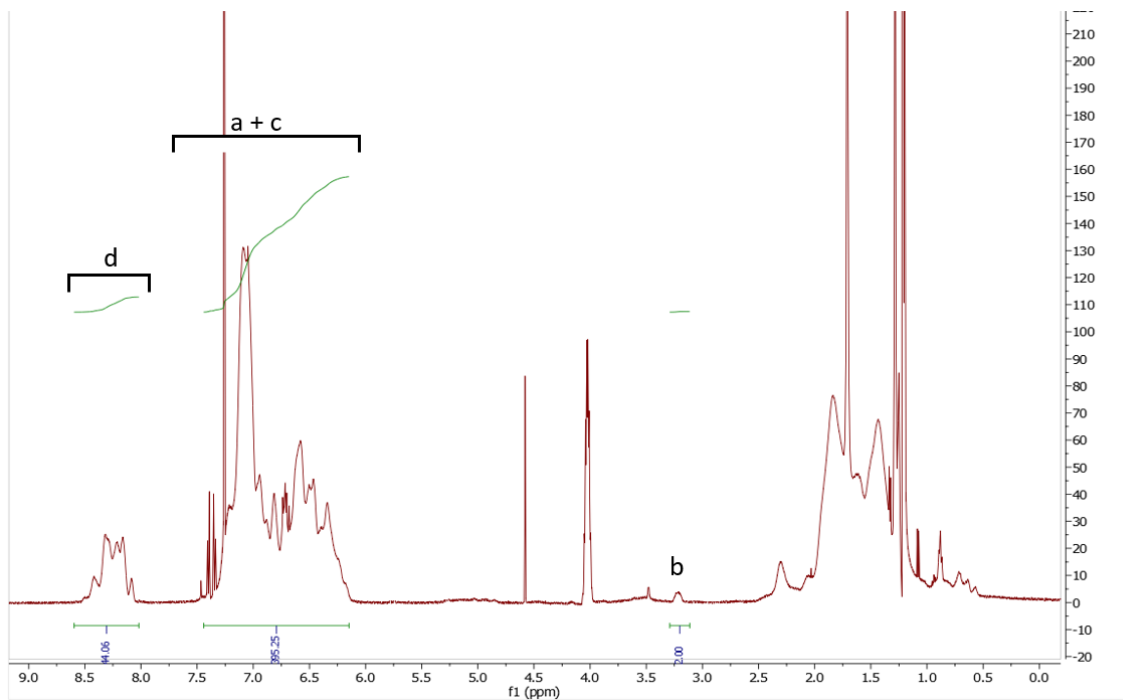


Figure A.13: NMR spectrum for BB₄. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer. See Figure A.7 for BB₄ structure.

A.2 Gel Permeation Chromatography (GPC)

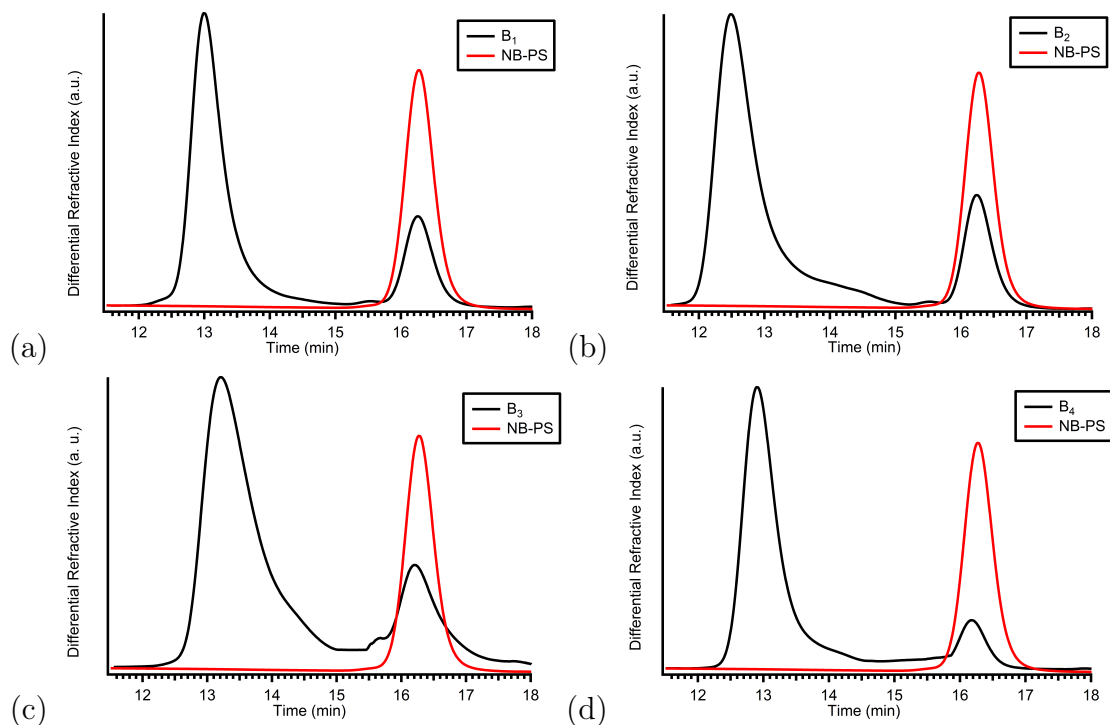


Figure A.14: GPC traces for BB-(PS-co-CTA) for (a) B₁ (72% B₁ and 28% unincorporated PS), (b) B₂ (80% B₂ and 20% unincorporated PS), (c) B₃ (75% B₃ and 25% unincorporated PS), (d) B₄ (80% B₁ and 20% unincorporated PS). All materials have free (unincorporated) PS chains from PS that was not functionalized with NB.

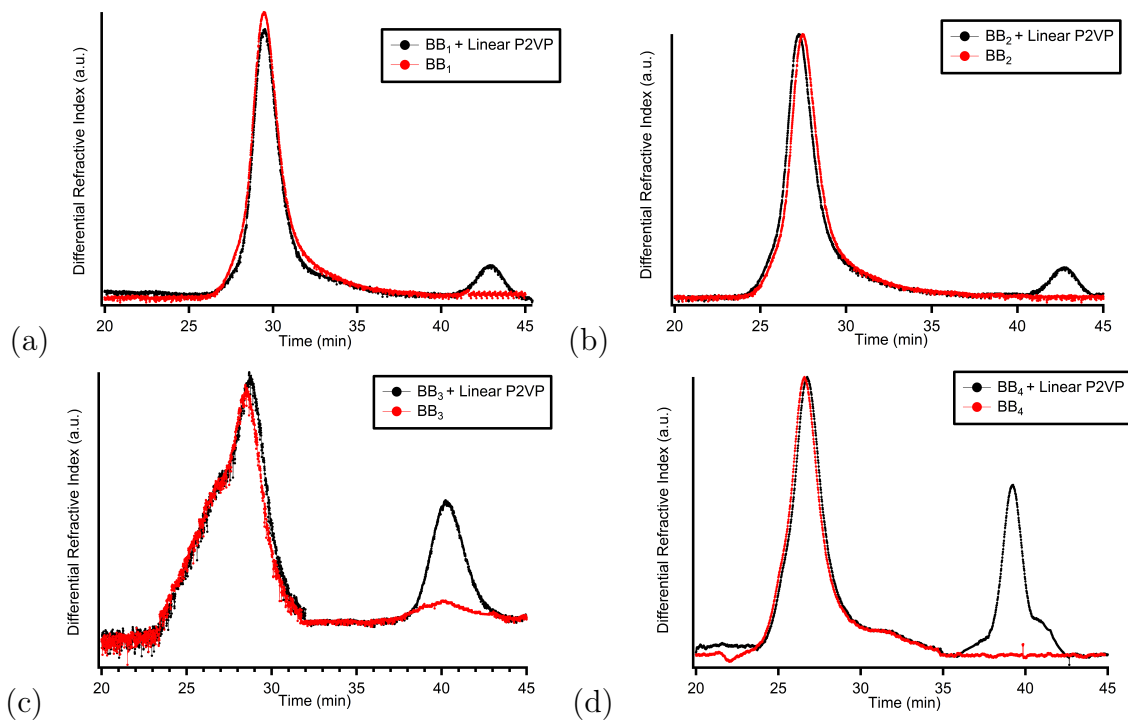


Figure A.15: Combined GPC traces for the mixture of BB-(PS-*co*-P2VP) with free linear P2VP chains and the final BB-(PS-*co*-P2VP) product. (a) BB₁; (b) BB₂; (c) BB₃; (d) BB₄.

A.3 Contact Angle Measurements

The fluids used on each surface are shown in Table [A.1](#). Thiodiglycol was omitted from measurements of the PS homopolymer as it was slightly inconsistent with the other fluids. (When included, the surface energy of PS is slightly reduced from 42.8 mN/m to 42.3 mN/m, and the uncertainty increases from ± 0.3 mN/m to ± 1.0 mN/m.) Water and ethylene glycol were omitted from measurements of P2VP as they fully spread on the surface. Note that both of these fluids can dissolve P2VP homopolymer. Water was also omitted for blend films when P2VP was at the surface (all as-cast films, certain annealed films), as these data were inconsistent with the OWRK model, presumably due to hydrogen bonding interactions. Ethylene glycol was omitted for blend films where the surface resembled PS, as these data were inconsistent with the OWRK trend. The reason for this inconsistency is unclear.

Table A.1: List of test fluids used for surface energy calculations for pure PS, pure P2VP, as-cast films for all blends and annealed films for all blends, (X) indicates test fluid used for surface energy measurements and (-) indicates test fluids not used for surface energy measurements.

Blends	Diiodomethane	Thiodiglycol	Ethylene glycol	Glycerol	Water
PS	X	-	X	X	X
P2VP	X	X	-	X	-
S1 As-cast	X	X	X	X	-
S3 As-cast	X	X	X	X	-
S5 As-cast	X	X	X	X	-
S7 As-cast	X	X	X	X	-
S11 As-cast	X	X	-	X	X
S15 As-cast	X	X	X	X	-
S16 As-cast	X	X	X	X	-
S17 As-cast	X	X	X	X	-
S18 As-cast	X	X	X	X	-
S1 Annealed	X	X	-	X	X
S3 Annealed	X	X	-	X	X
S5 Annealed	X	X	-	X	X
S7 Annealed	X	X	-	X	X
S11 Annealed	X	X	-	X	X
S15 Annealed	X	X	X	X	-
S16 Annealed	X	X	X	X	-
S17 Annealed	X	X	-	X	X
S18 Annealed	X	X	-	X	X

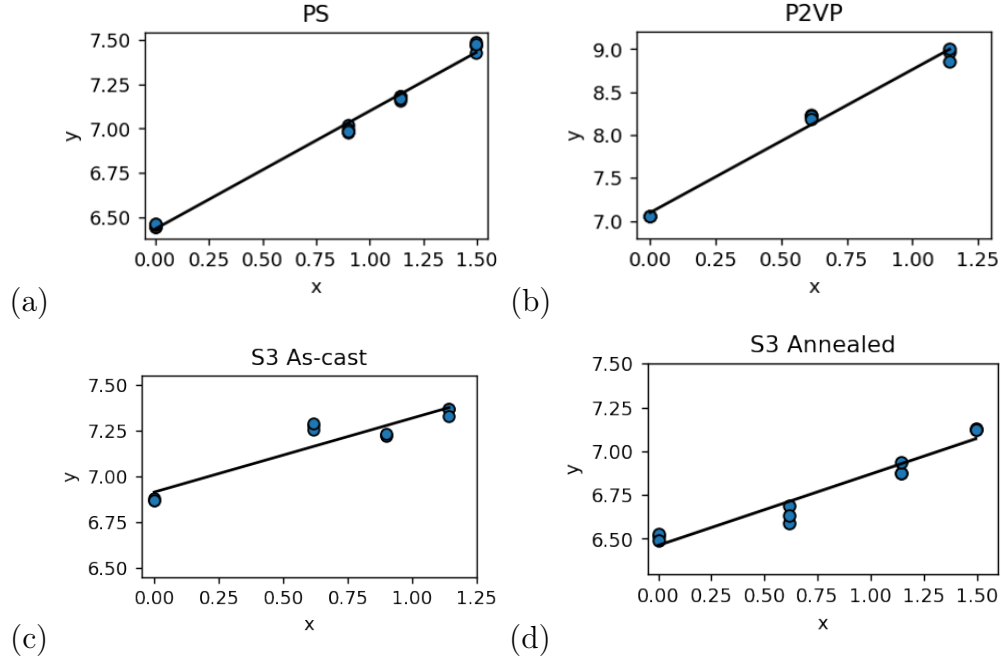


Figure A.16: OWRK fit for contact angle of (a) PS ($\gamma_s = 41.87 \pm 0.19$, $\gamma_s^d = 41.43 \pm 0.18$, $\gamma_s^p = 0.43 \pm 0.02$) (b) P2VP ($\gamma_s = 53.15 \pm 0.70$, $\gamma_s^d = 50.36 \pm 0.67$, $\gamma_s^p = 2.77 \pm 0.21$) (c) Sample S3 as-cast ($\gamma_s = 48.20 \pm 0.83$, $\gamma_s^d = 48.03 \pm 0.83$, $\gamma_s^p = 0.16 \pm 0.04$) (d) Sample S3 annealed ($\gamma_s = 41.67 \pm 0.67$, $\gamma_s^d = 41.43 \pm 0.67$, $\gamma_s^p = 0.23 \pm 0.05$). Surface energy units = mN/m.

Figure A.16 shows examples of the nonlinear regression analysis for four samples.

A.4 Microscopy and TOF-SIMS

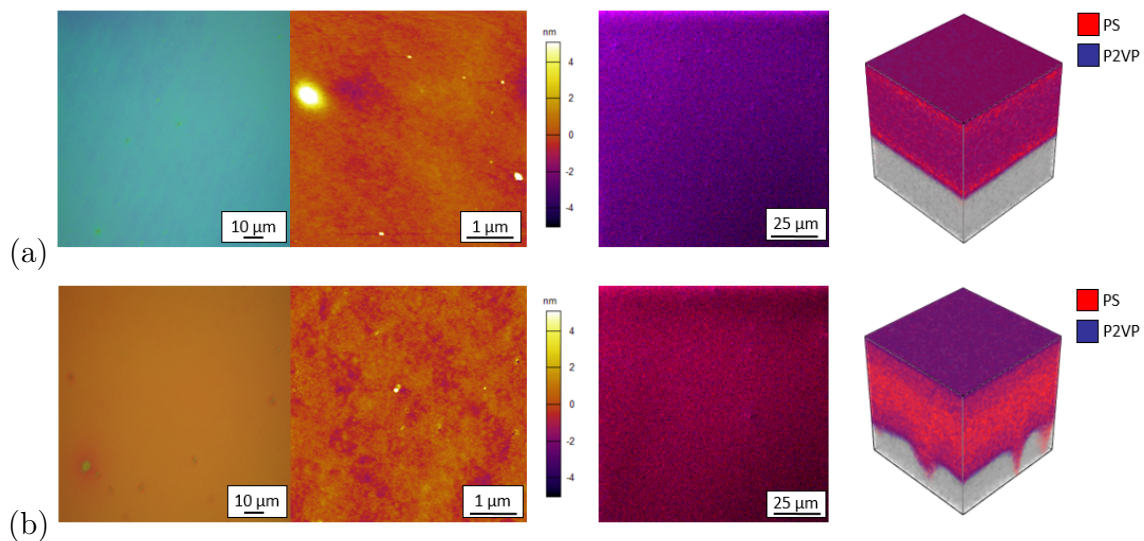


Figure A.17: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S16 (BB₂/PS₃) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

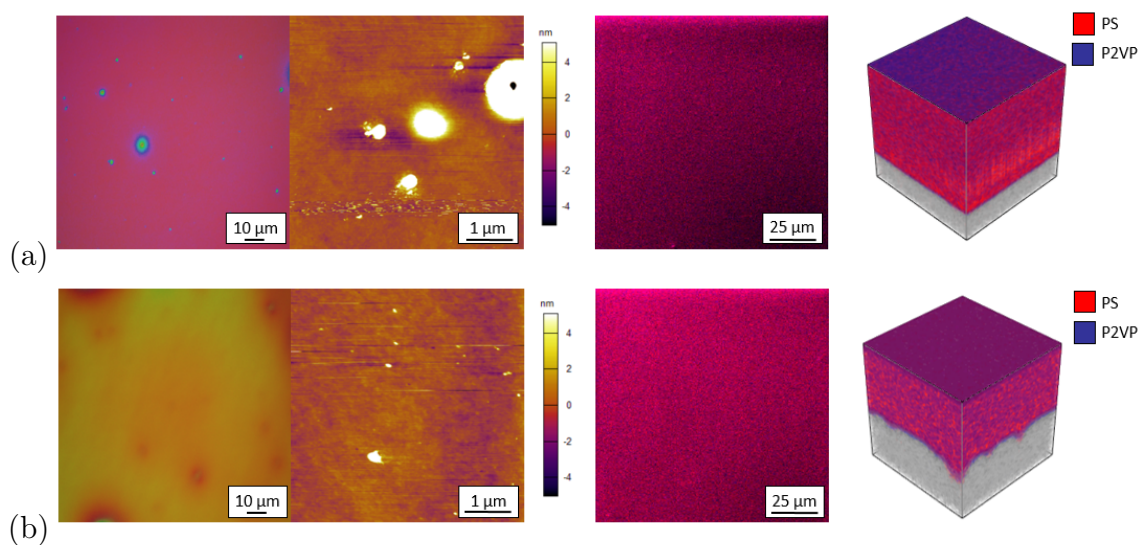


Figure A.18: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S17 (BB₃/PS₃) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

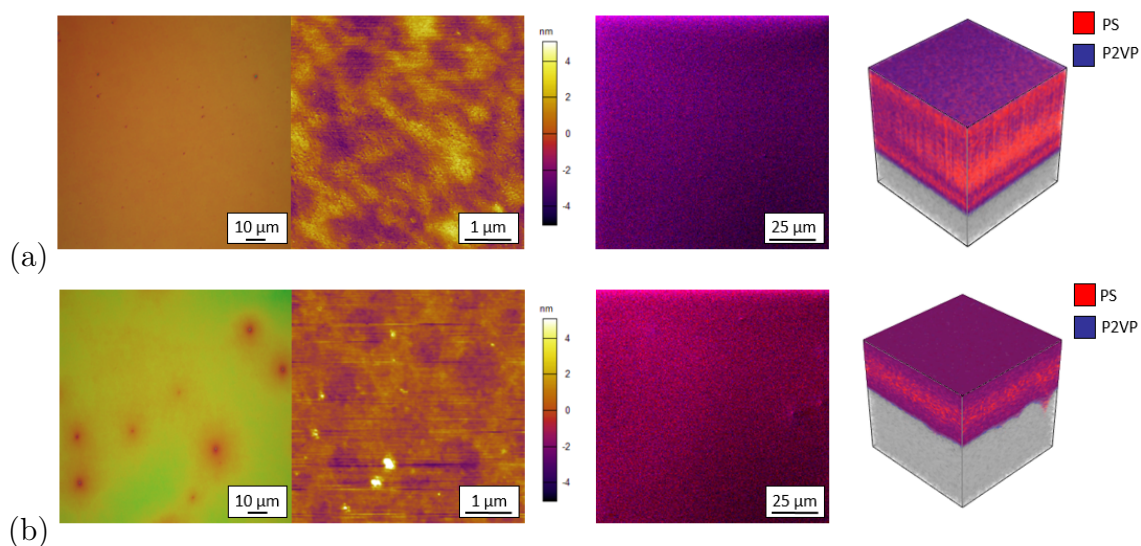


Figure A.19: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image, for blend S18 (BB₄/PS₃) (a) as-cast and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

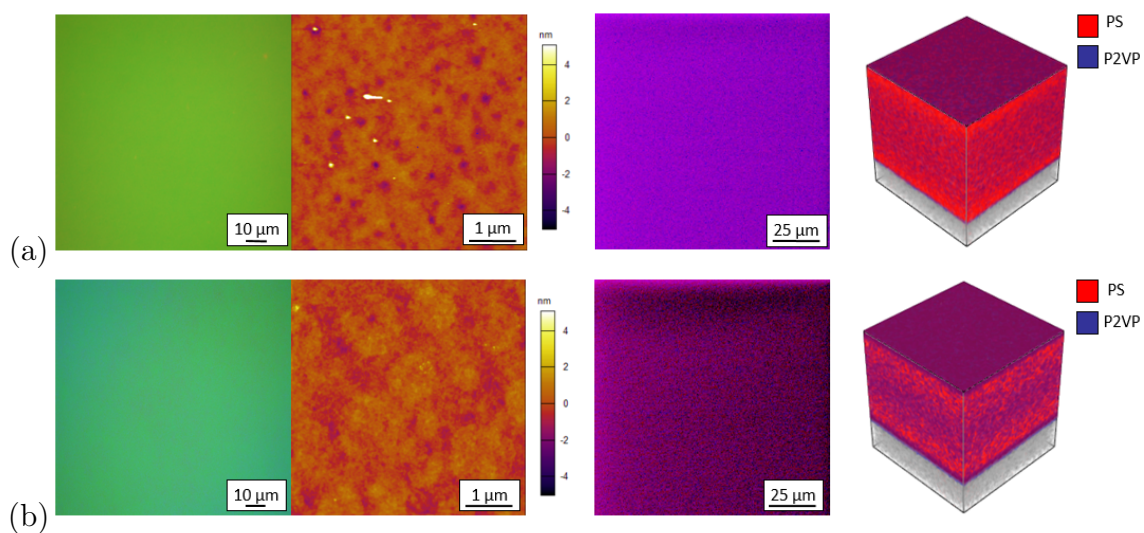


Figure A.20: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S1 (BB_1/PS_1) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

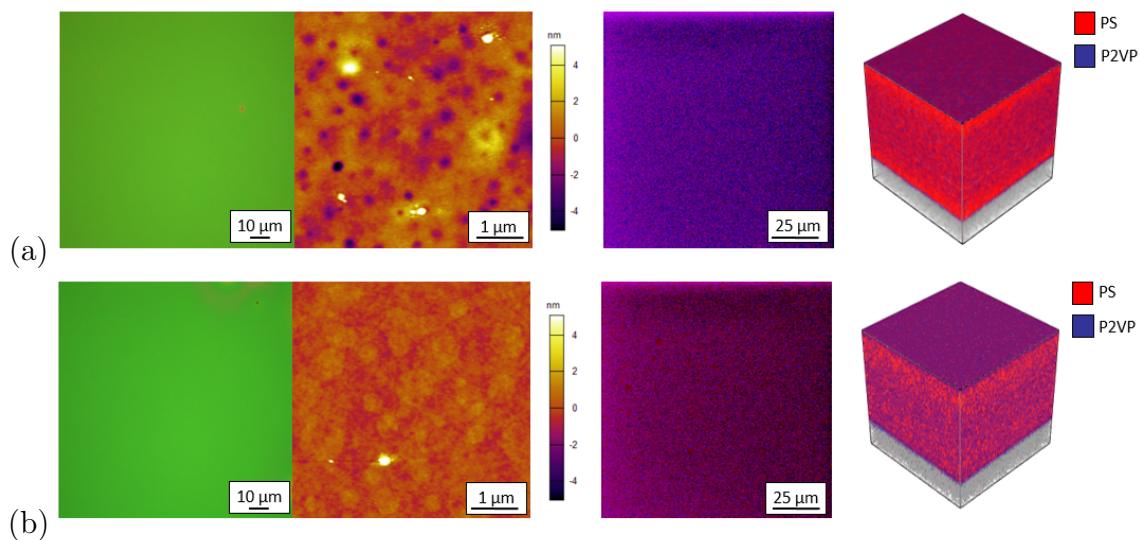


Figure A.21: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S3 (BB_2/PS_1) (a) as-cast from chlorobenzene and (b) annealed at 140 °C for 48 hrs in a nitrogen-filled glove box. Gray slab in the 3D TOF-SIMS image is the Silicon substrate.

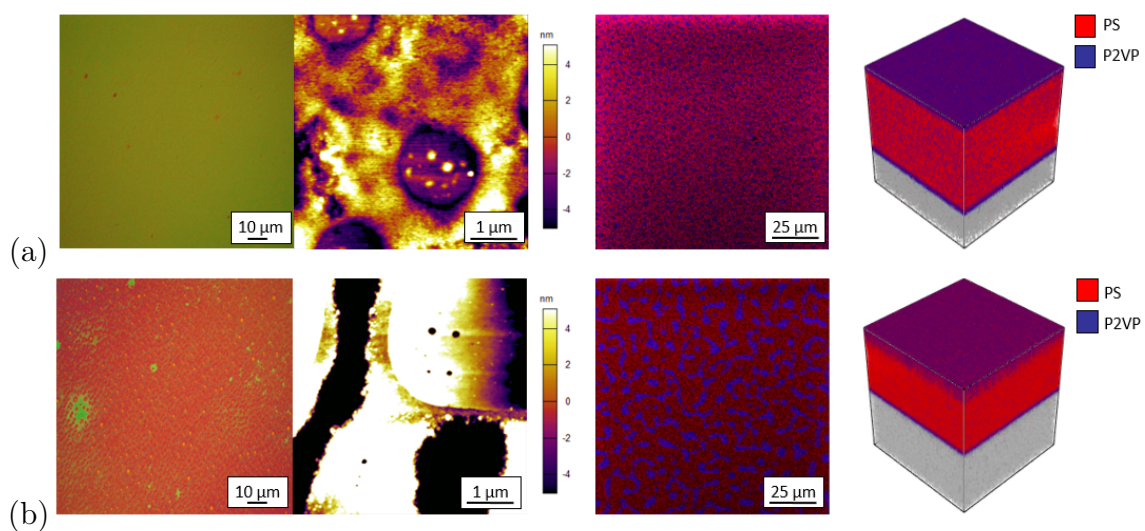


Figure A.22: From left to right: OM, AFM, 2D TOF-SIMS image of the surface, and 3D TOF-SIMS image for blend S5 (BB_3/PS_1) (a) as-cast and (b) annealed at 140 °C for 48 hrs. Gray slab in the 3D TOF-SIMS image is the silicon substrate.

A.5 Linear P2VP/Linear PS Blends

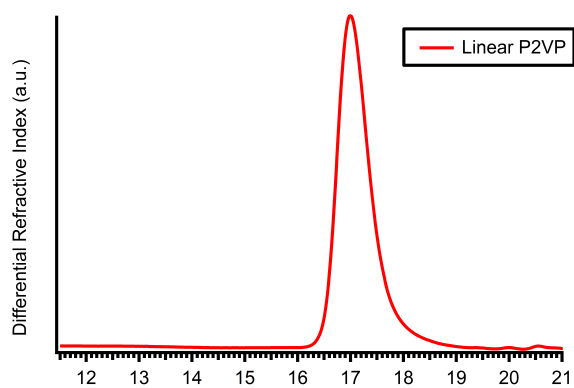


Figure A.23: GPC trace for Linear P2VP.

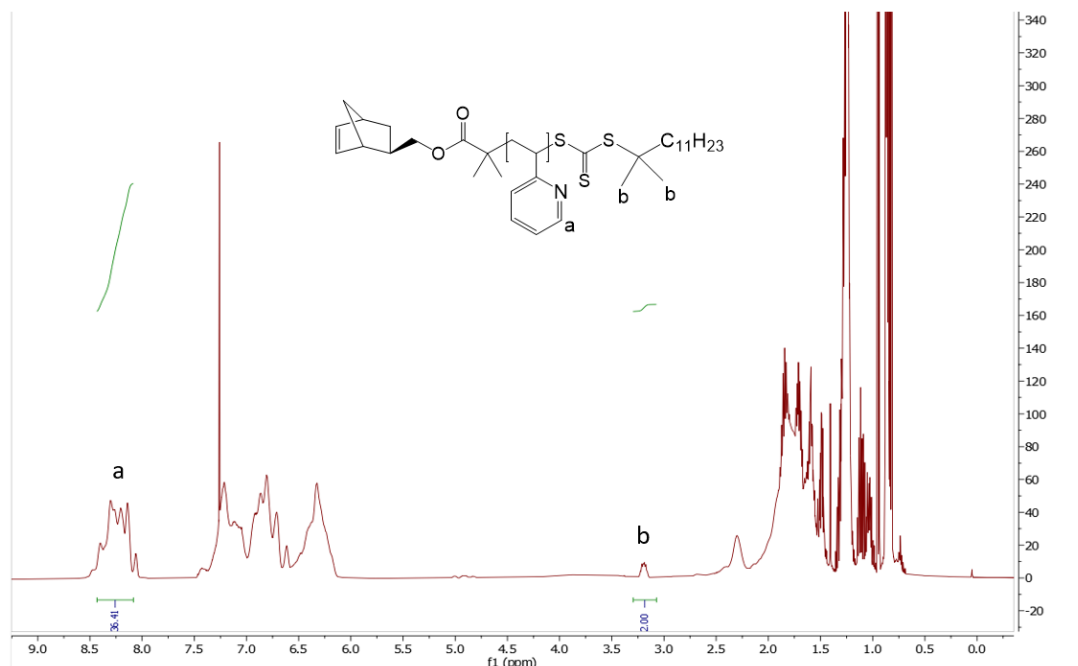


Figure A.24: NMR spectrum for low molecular weight linear P2VP.

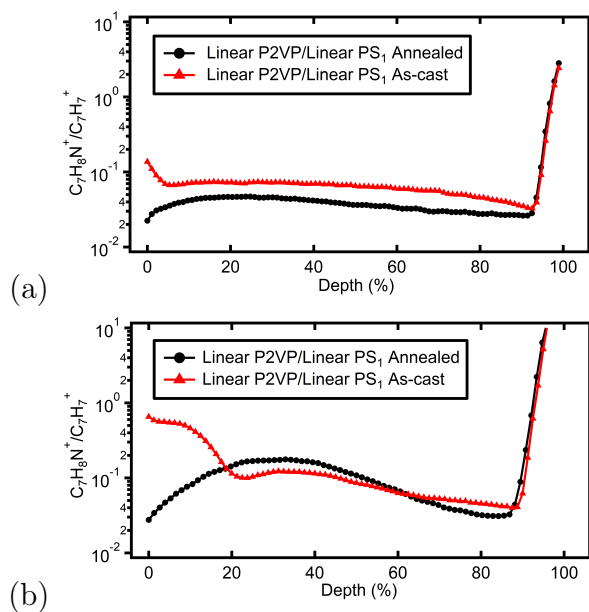


Figure A.25: TOF-SIMS depth profiles for thin films of Linear P2VP/Linear PS₁, both as-cast and annealed, for (a) 2 wt% P2VP and (b) 10 wt% P2VP. The ratio of C₇C₈N⁺ to C₇H₇⁺ signals is proportional to the concentration of P2VP. The polymer-air interface is at depth = 0 % and the polymer-substrate interface is at depth = 100 %.

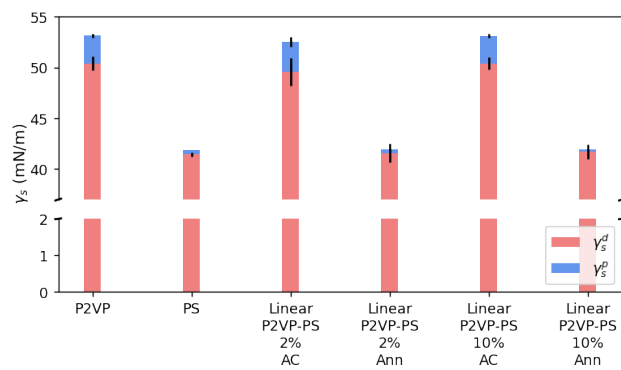


Figure A.26: Surface energies for thin film blends of Linear P2VP/Linear PS₁, as-cast and annealed at 140 °C for 48 hours. Blends with 2 wt% and 10 wt% loading of P2VP.

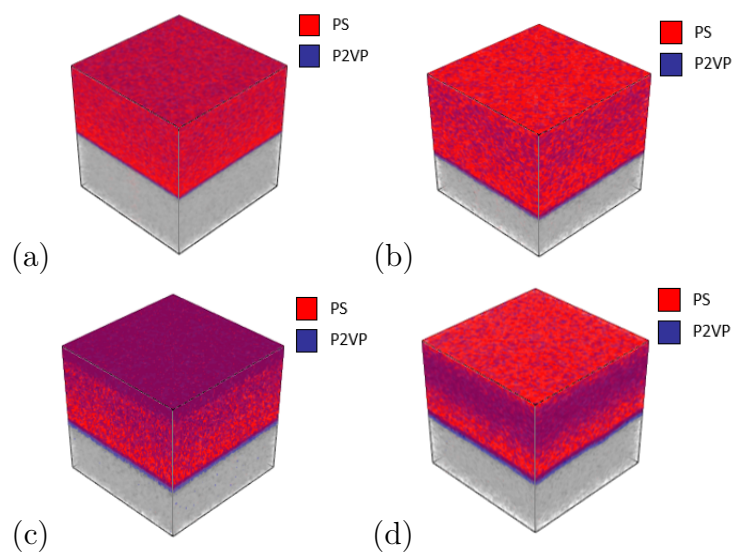


Figure A.27: 3D TOF-SIMS images for blends of Linear P2VP/Linear PS₁, 2 wt% P2VP, (a) as-cast and (b) annealed at 140 °C for 48 hours. 3D TOF-SIMS images for blends of Linear P2VP/Linear PS, 10 wt% P2VP, (c) as-cast and (d) annealed at 140 °C for 48 hours.

Appendix B

Supplemental Characterization for: Surface Properties of Thin Films of Bottlebrush Statistical Copolymers.

B.1 ^1H NMR

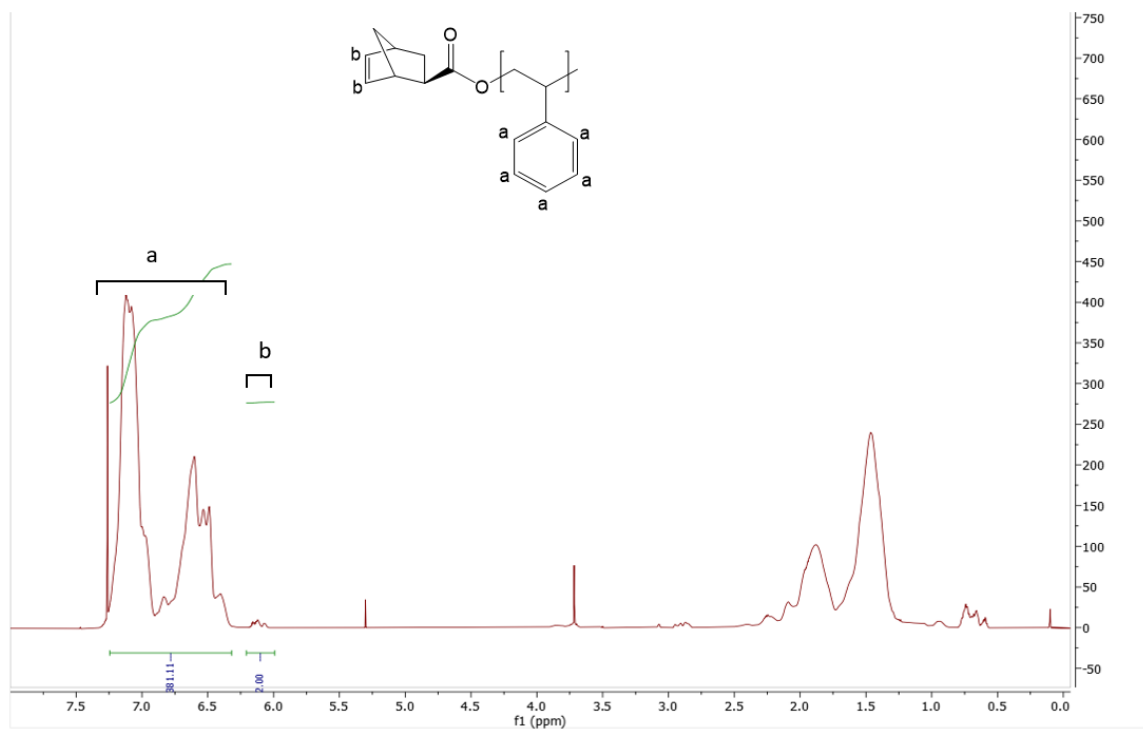


Figure B.1: NMR spectrum for NB-PS39.

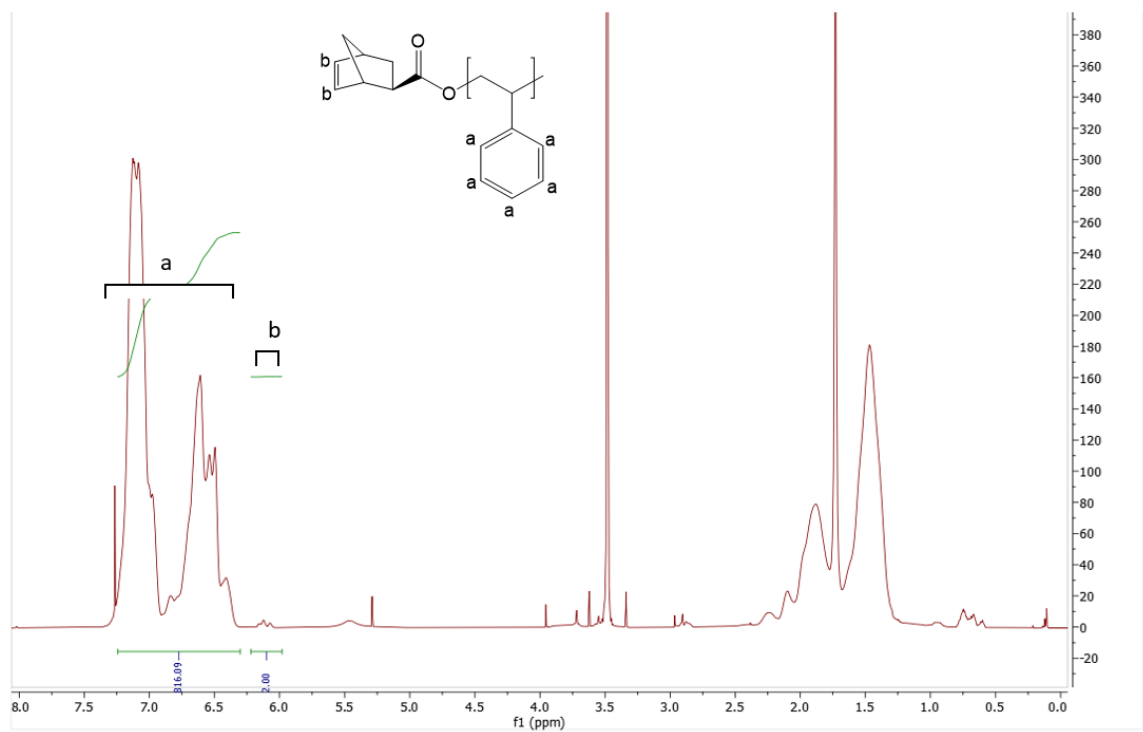


Figure B.2: NMR spectrum for NB-PS96.

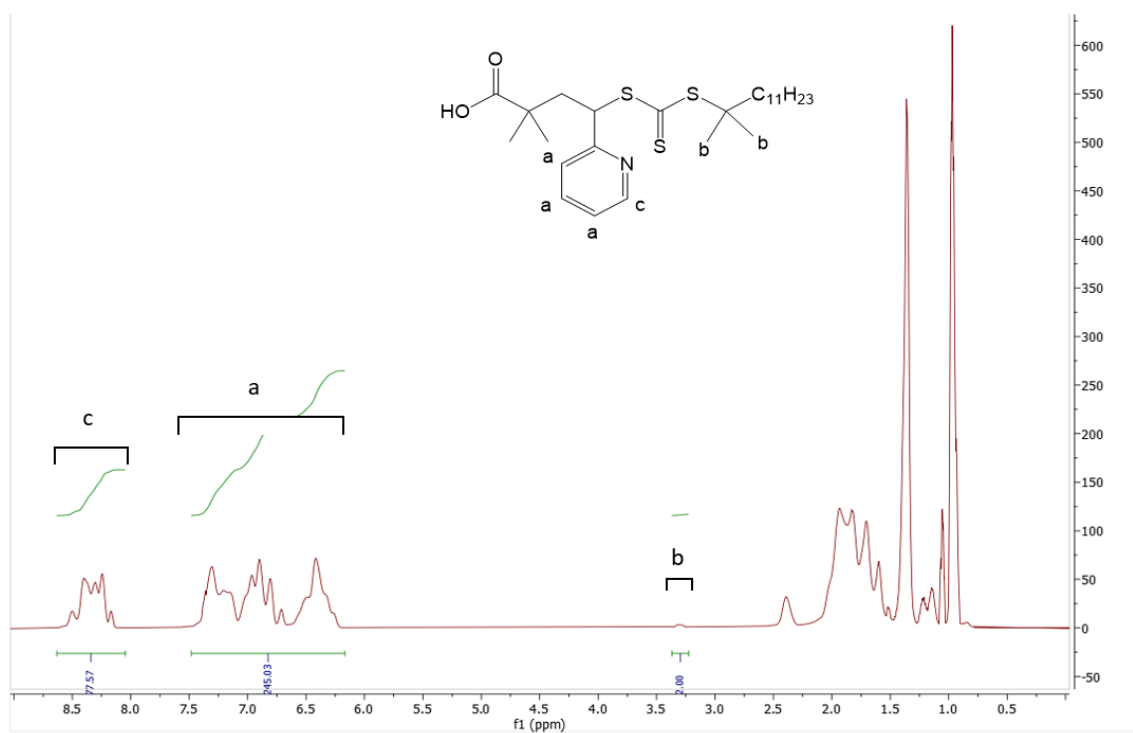


Figure B.3: NMR spectrum for P2VP macromolecule. The protons from 2-vinylpyridine (a, 3H, 6.3-7.3 PPM; c, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n .

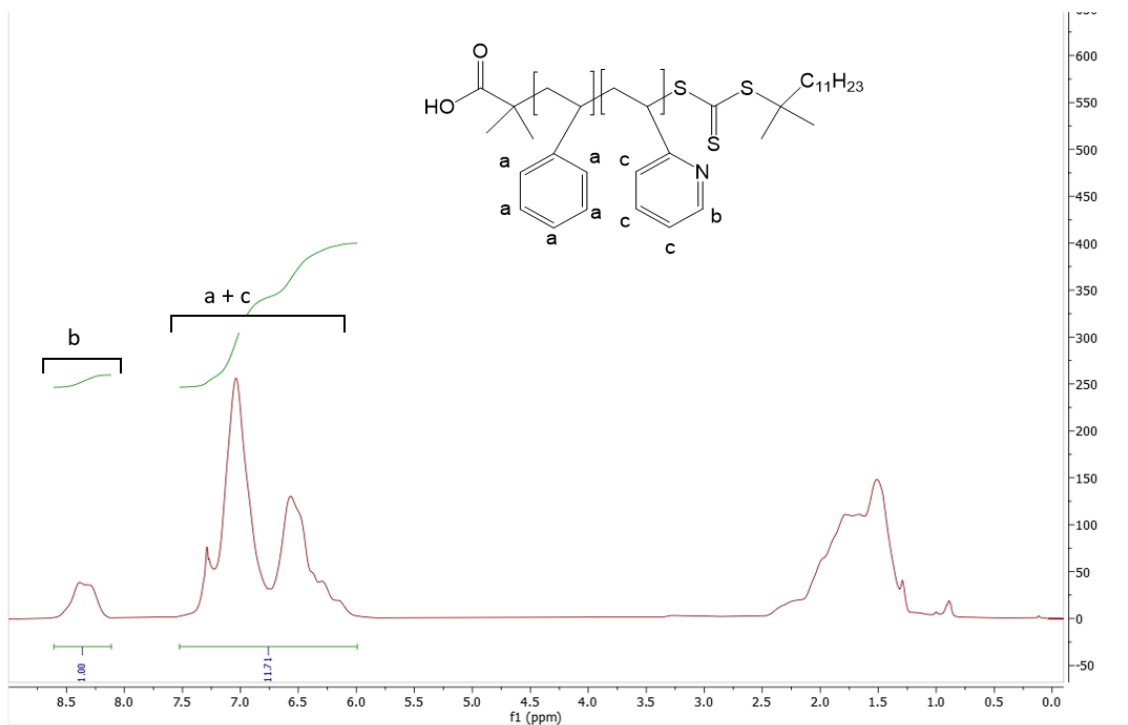


Figure B.4: NMR spectrum for P(S-co-2VP)₁. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer.

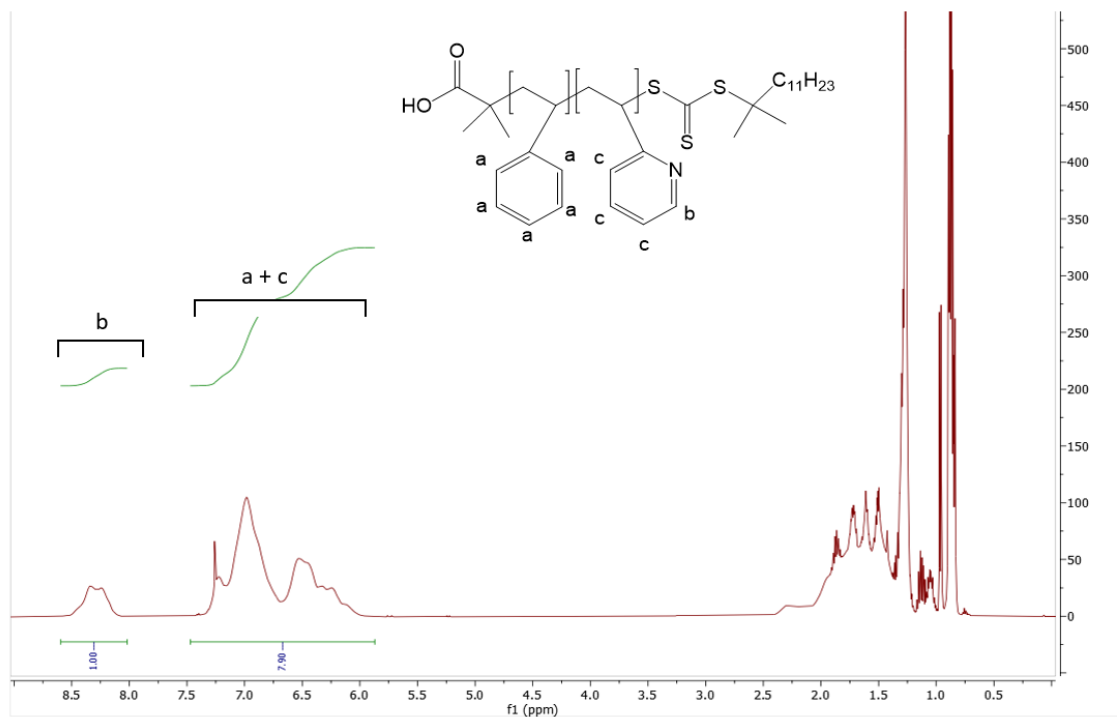


Figure B.5: NMR spectrum for P(S-co-2VP)₂. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer

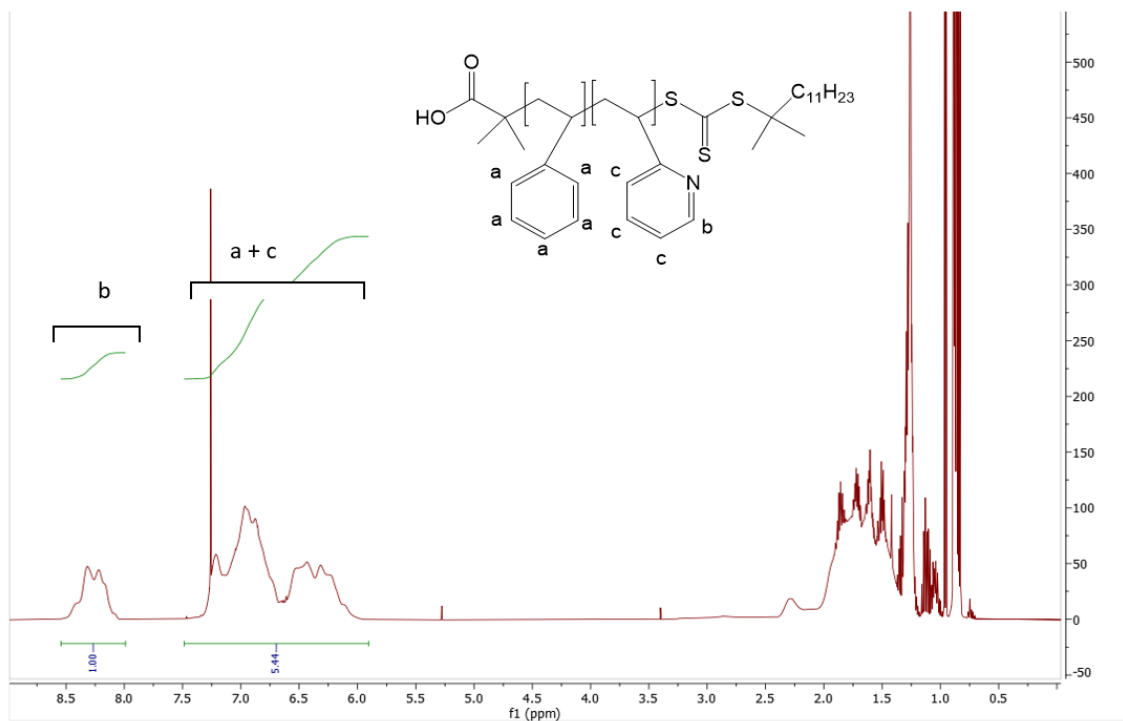


Figure B.6: NMR spectrum for P(S-co-2VP)₃. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer

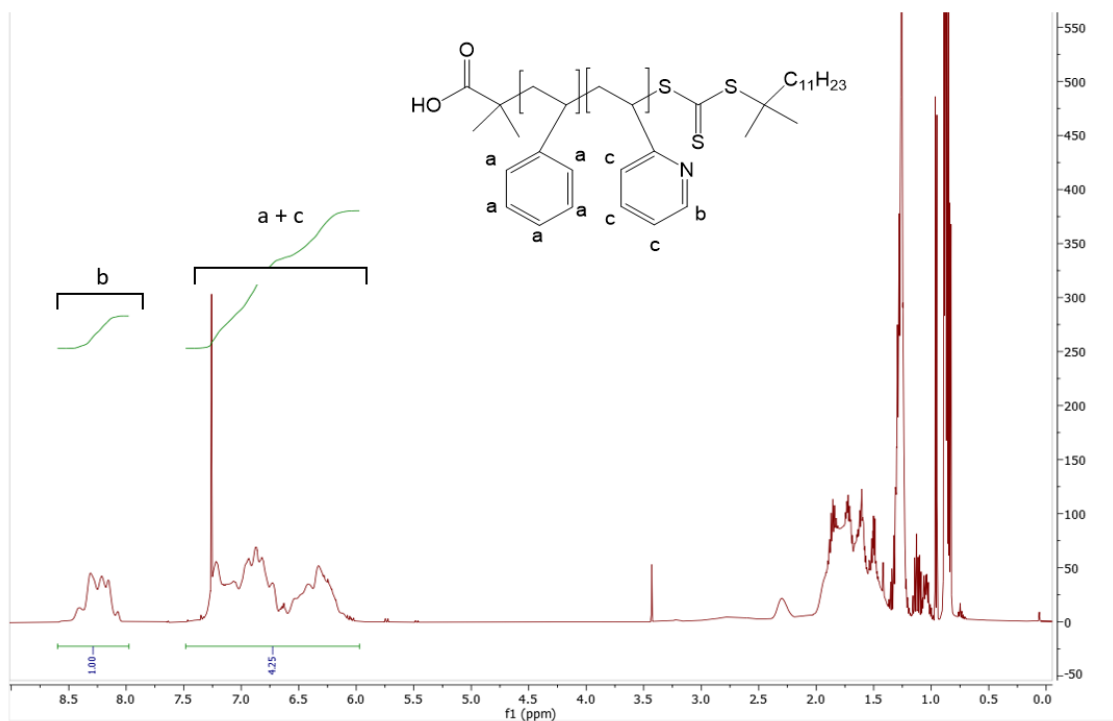


Figure B.7: NMR spectrum for P(S-co-2VP)₄. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM) were integrated relative to the proton from 2-vinylpyridine (b, 1H, 7.9 - 8.4 ppm) to obtain mole percent of each polymer

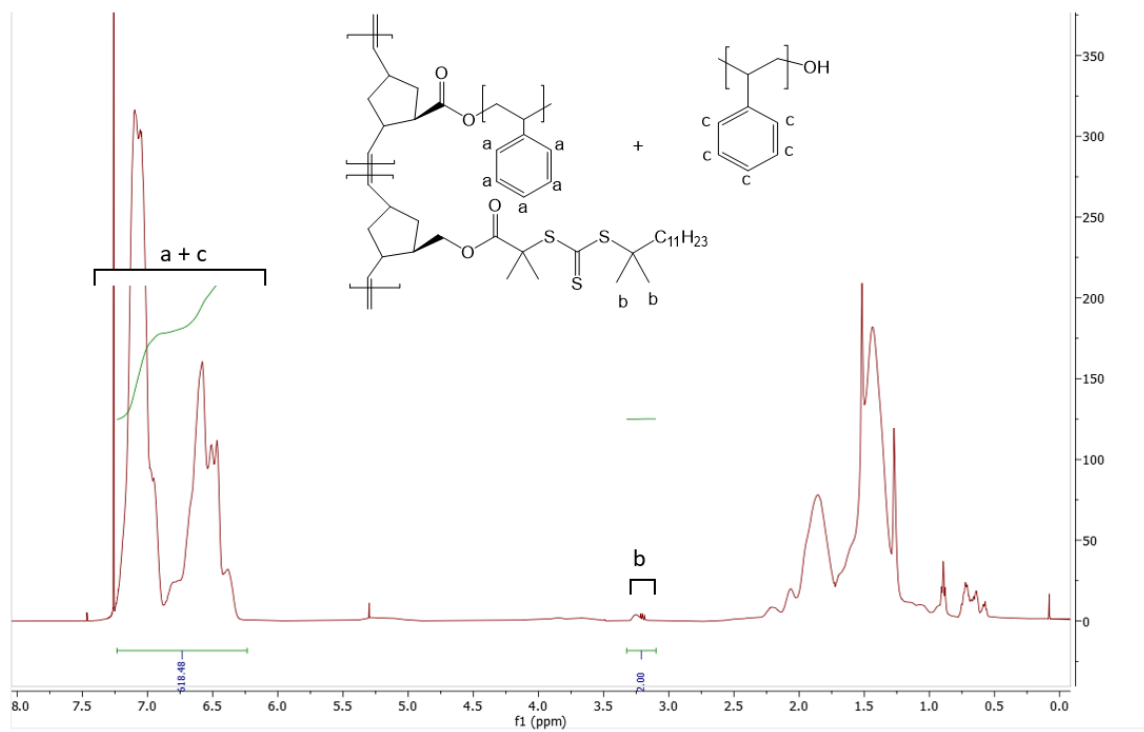


Figure B.8: NMR spectrum for B_{5,6,7}. The protons from styrene in bottlebrush (a, 5H, 6.25-7.3 ppm) and styrene from unreacted polystyrene (c, 5H, 6.25-7.3 ppm) were integrated relative to the proton from CTA (b, 2H, 3.25 ppm) to obtain mole percent of each polymer.

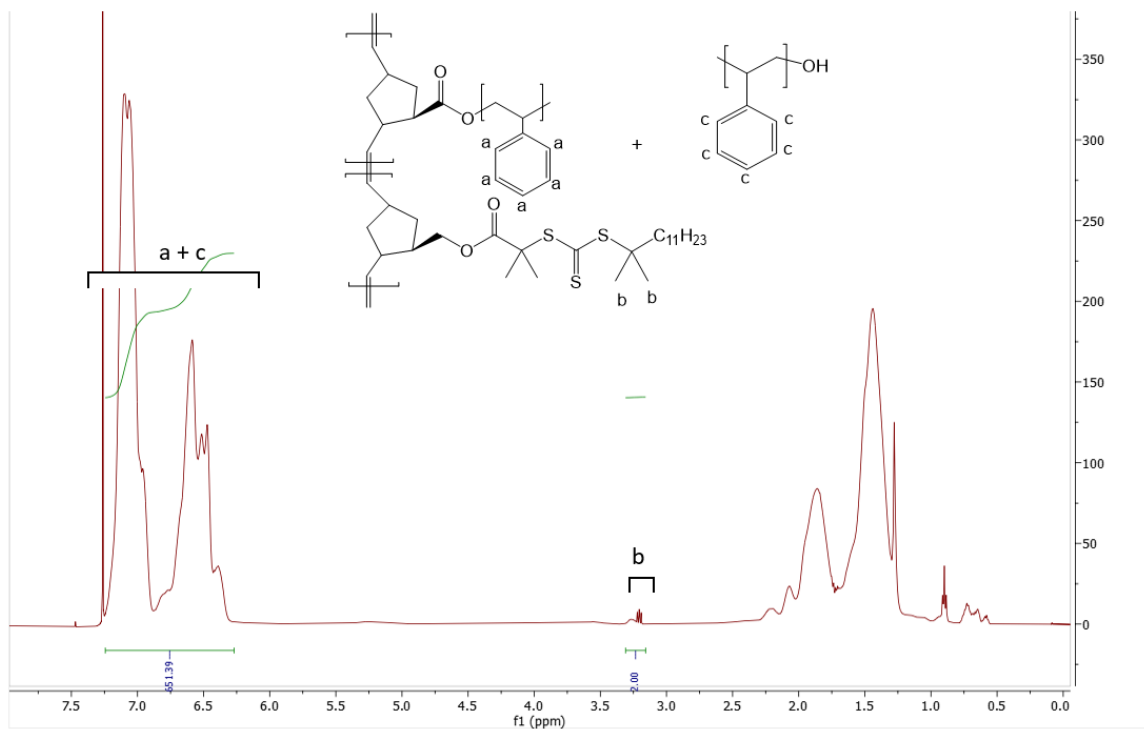


Figure B.9: NMR spectrum for B_{8,9,10}. The protons from styrene in bottlebrush (a, 5H, 6.25-7.3 ppm) and styrene from unreacted polystyrene (c, 5H, 6.25-7.3 ppm) were integrated relative to the proton from CTA (b, 2H, 3.25 ppm) to obtain mole percent of each polymer.

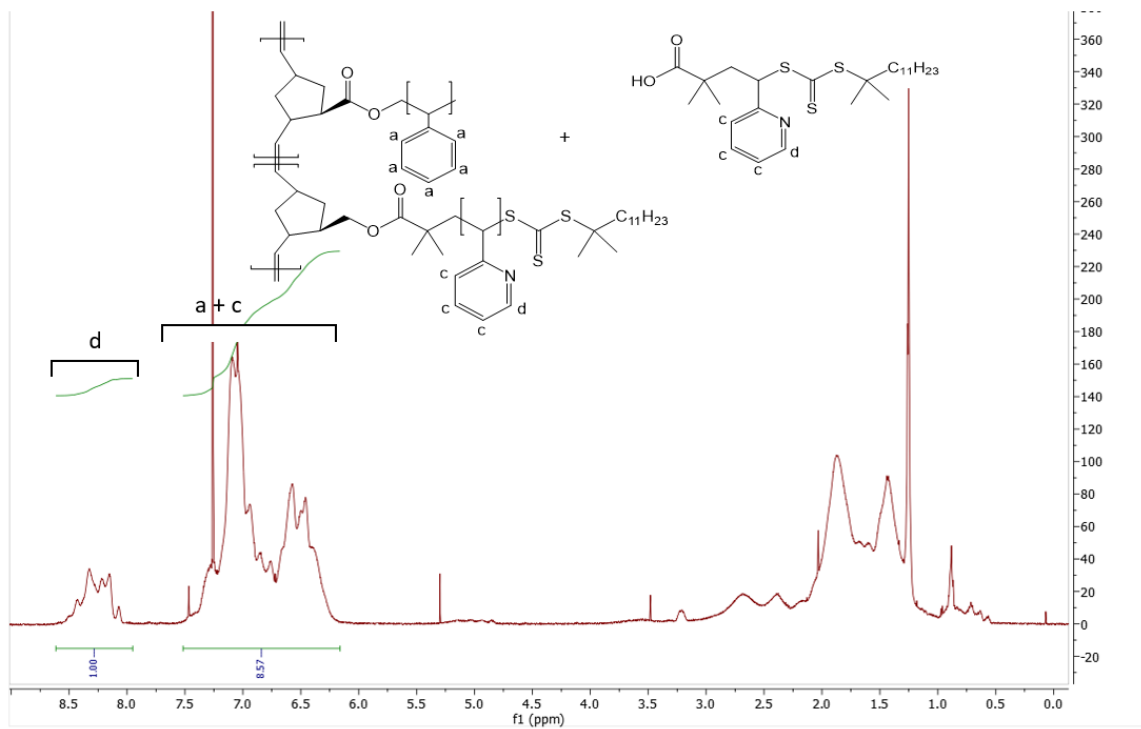


Figure B.10: NMR spectrum for BB₅ + Linear P2VP.

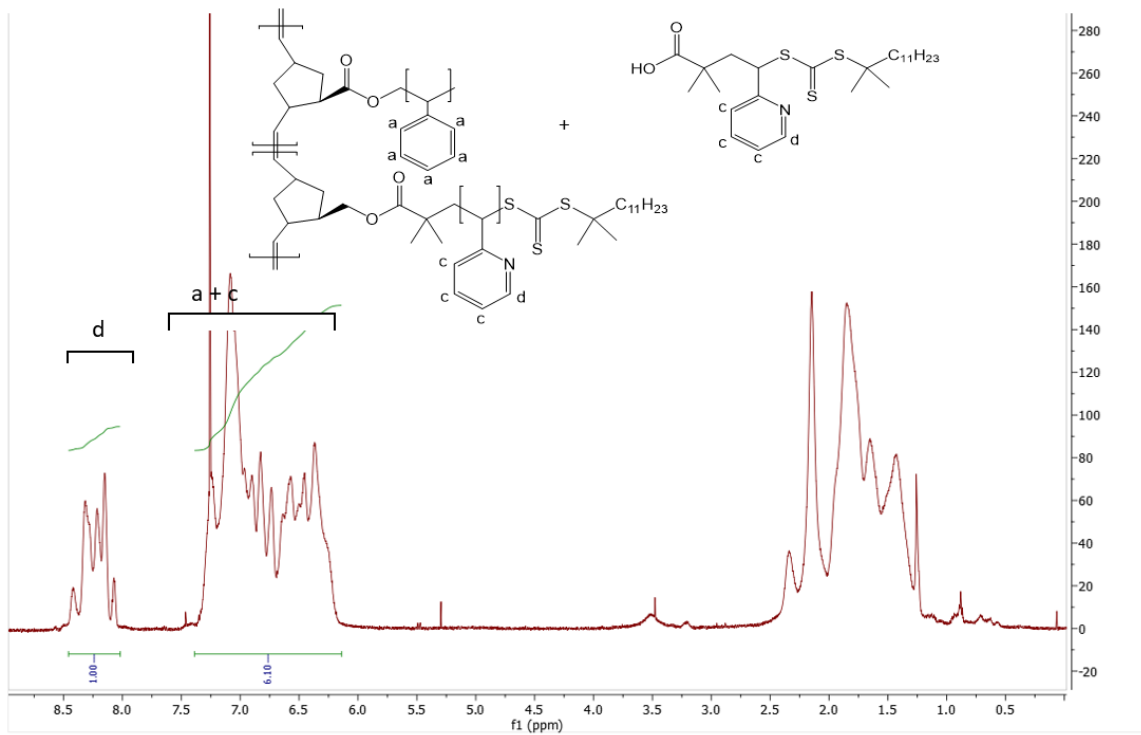


Figure B.11: NMR spectrum for BB₆ + Linear P2VP.

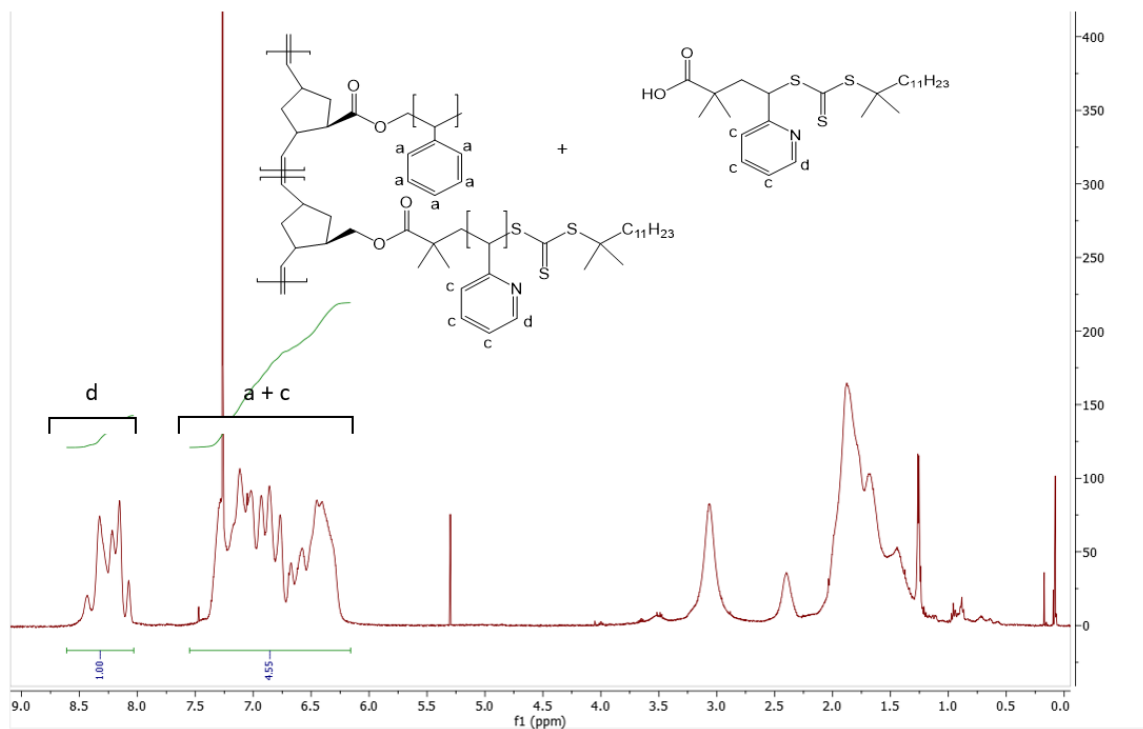


Figure B.12: NMR spectrum for BB₇ + Linear P2VP.

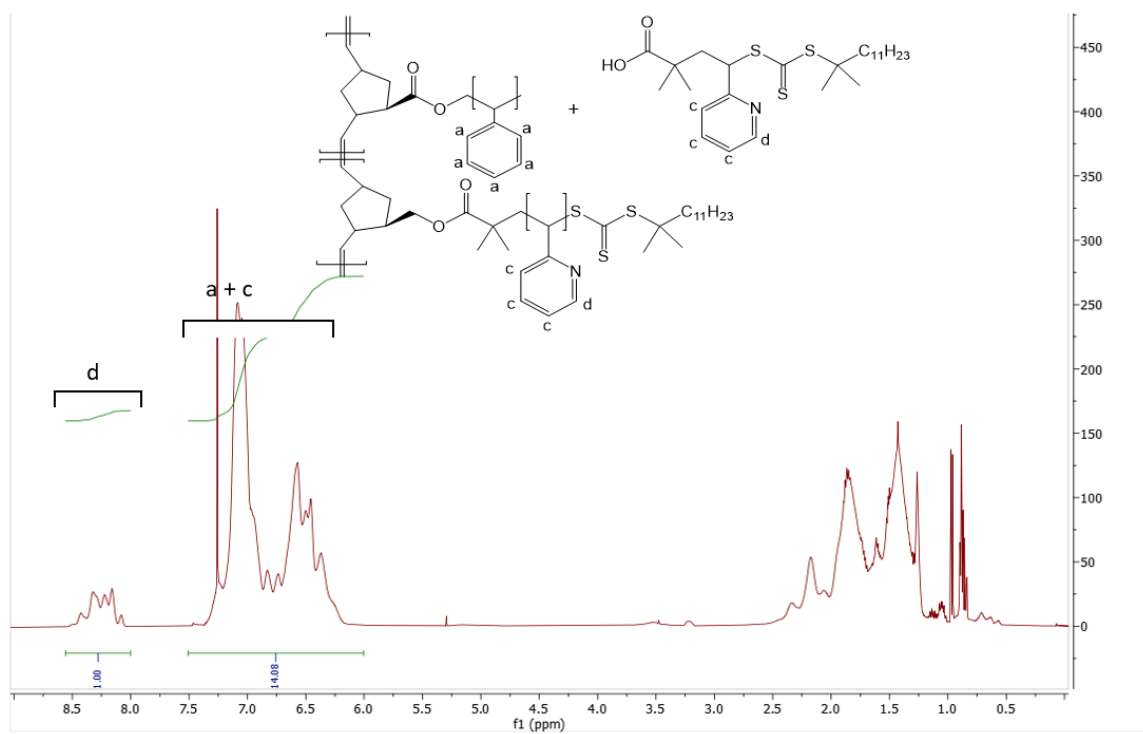


Figure B.13: NMR spectrum for BB₈ + Linear P2VP.

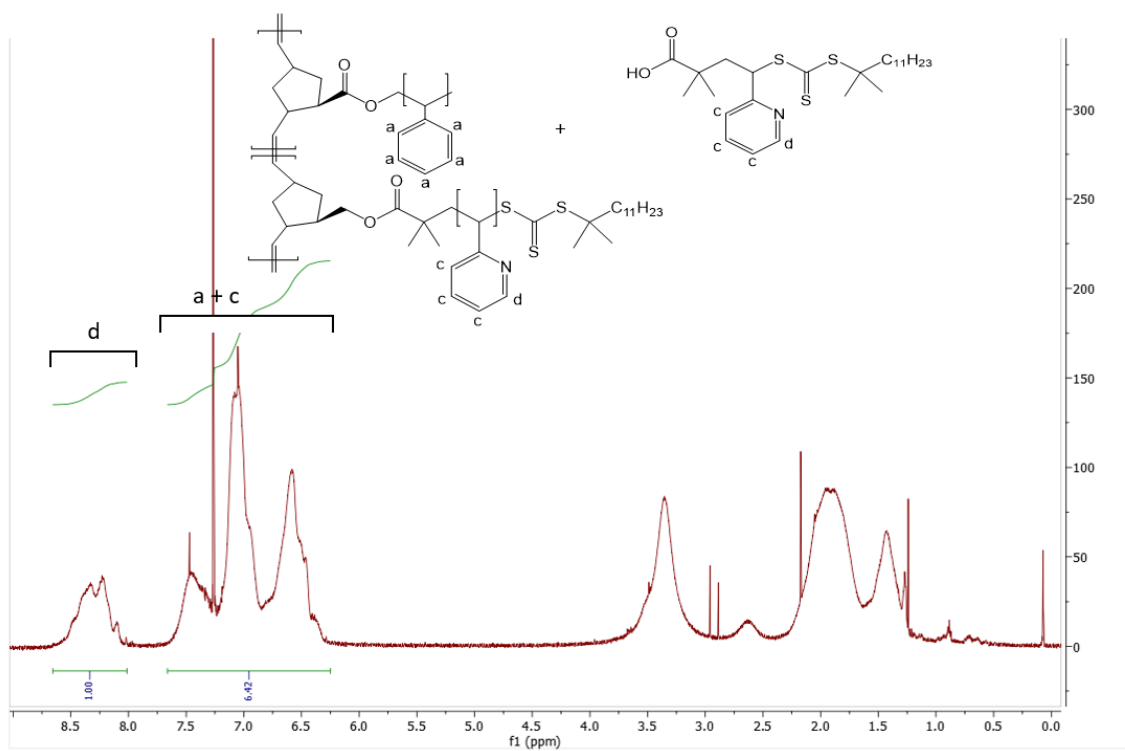


Figure B.14: NMR spectrum for BB₉ + Linear P2VP.

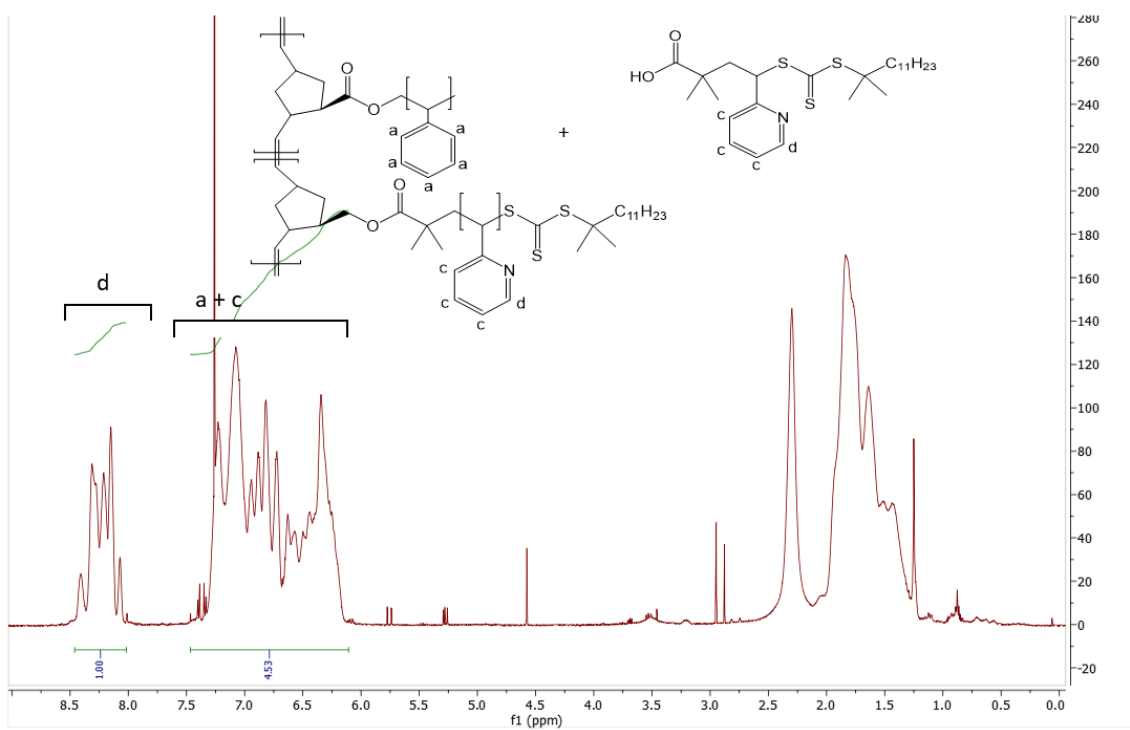


Figure B.15: NMR spectrum for BB₁₀ + Linear P2VP.

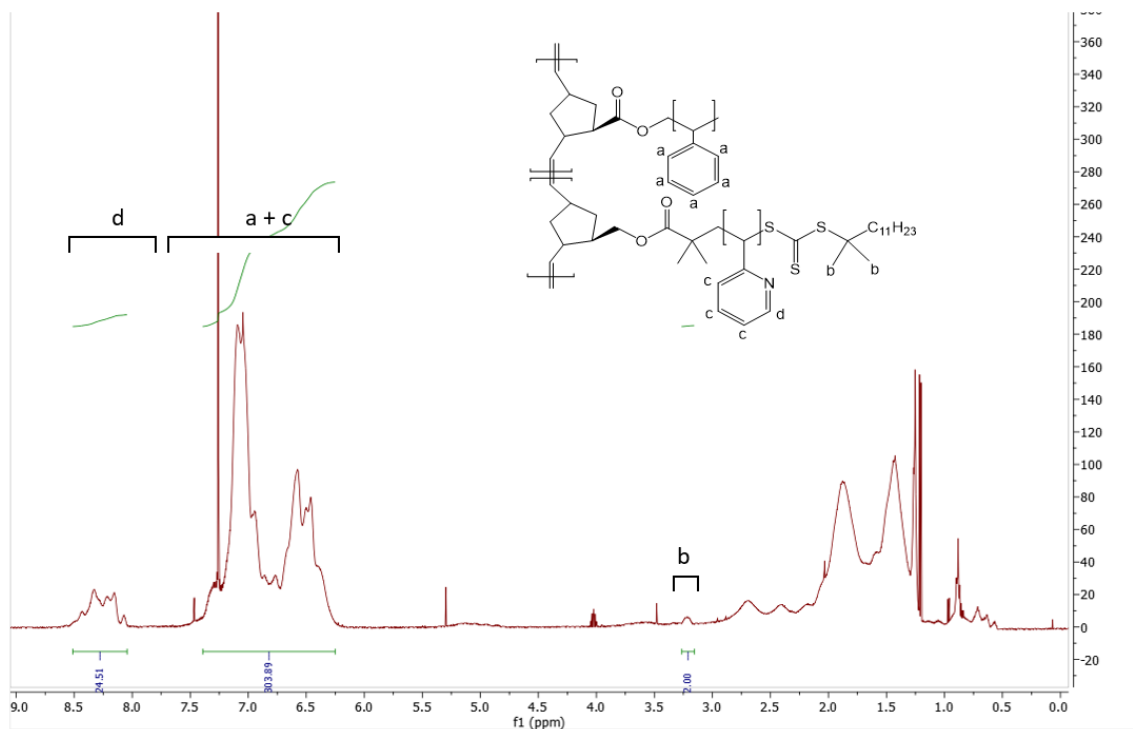


Figure B.16: NMR spectrum for BB₅. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

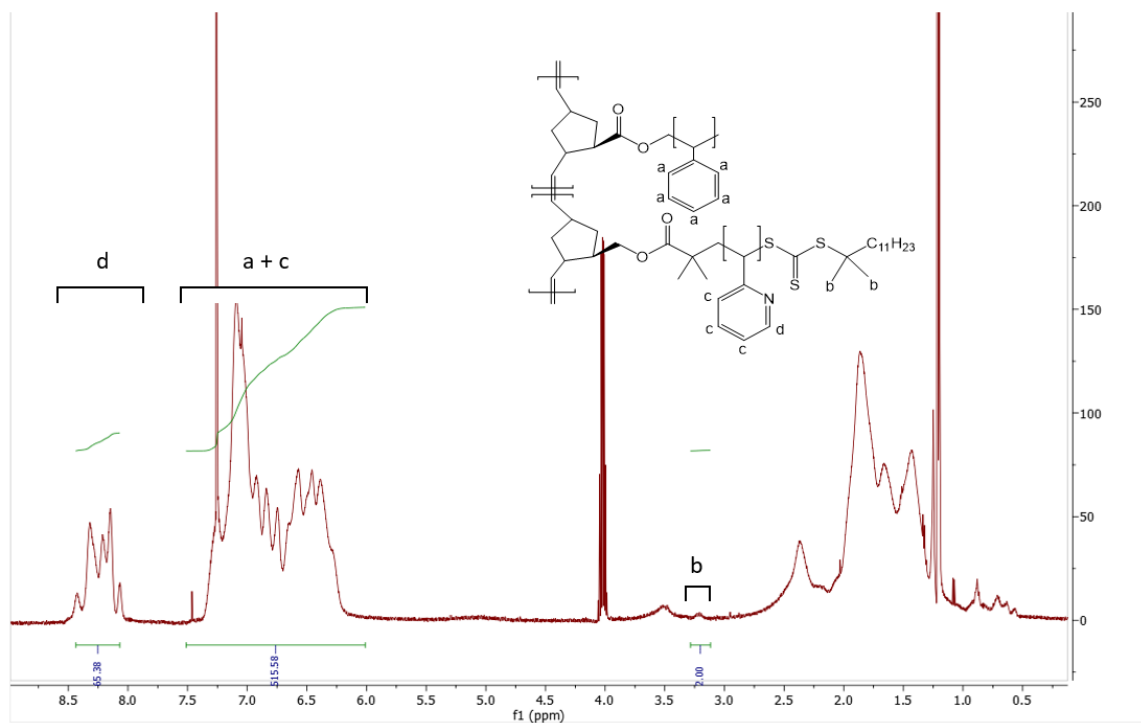


Figure B.17: NMR spectrum for BB₆. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

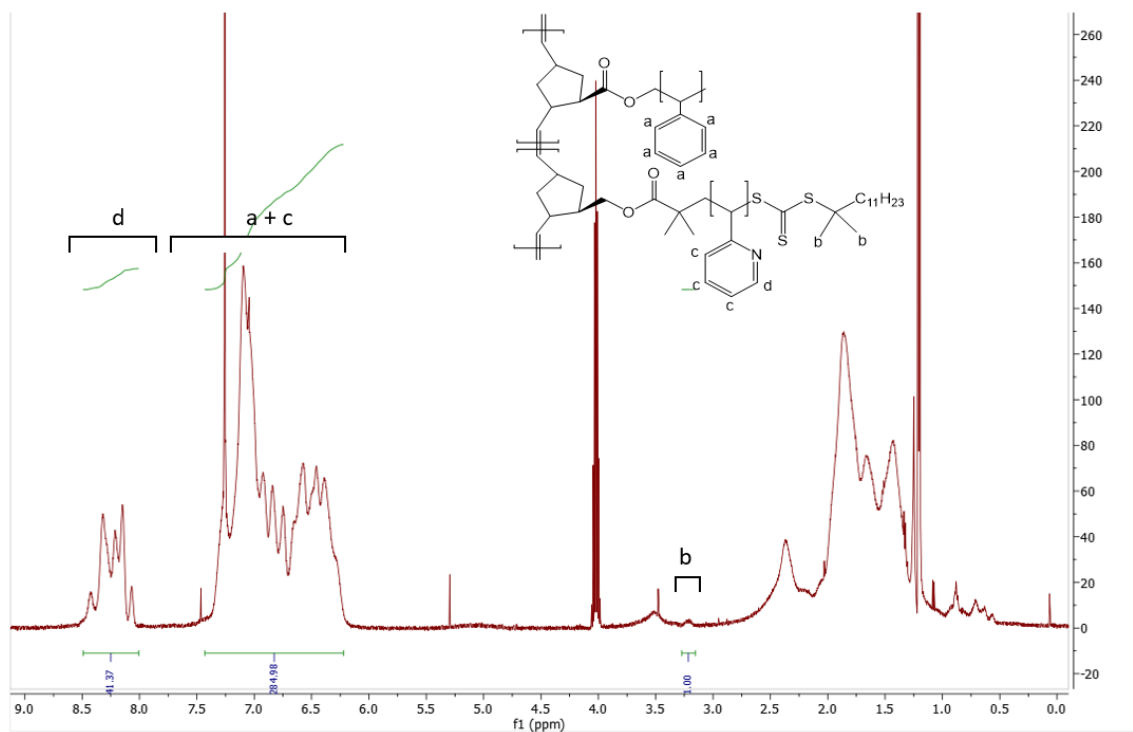


Figure B.18: NMR spectrum for BB₇. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

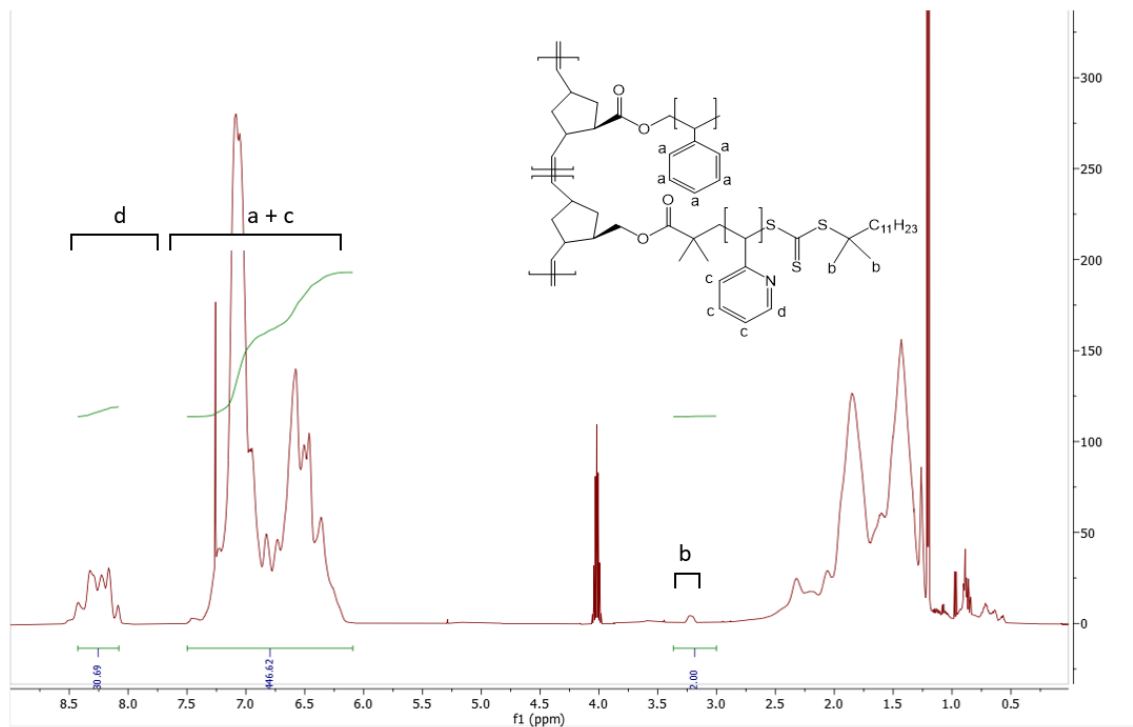


Figure B.19: NMR spectrum for BB₈. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

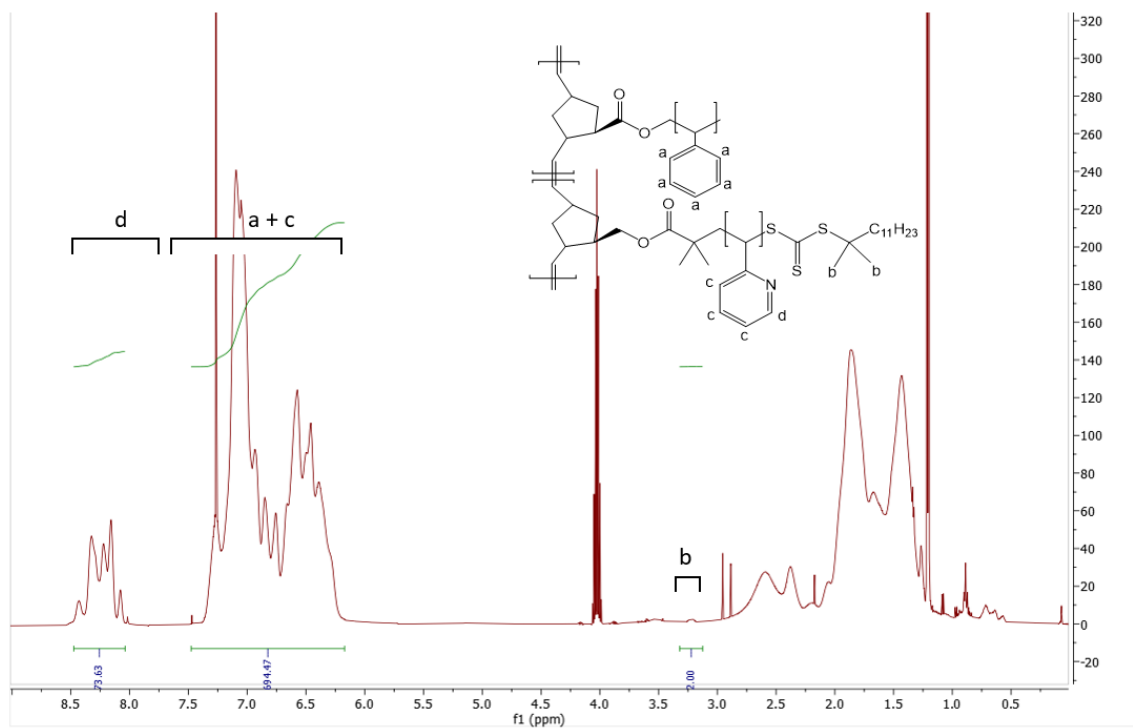


Figure B.20: NMR spectrum for BB₉. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer.

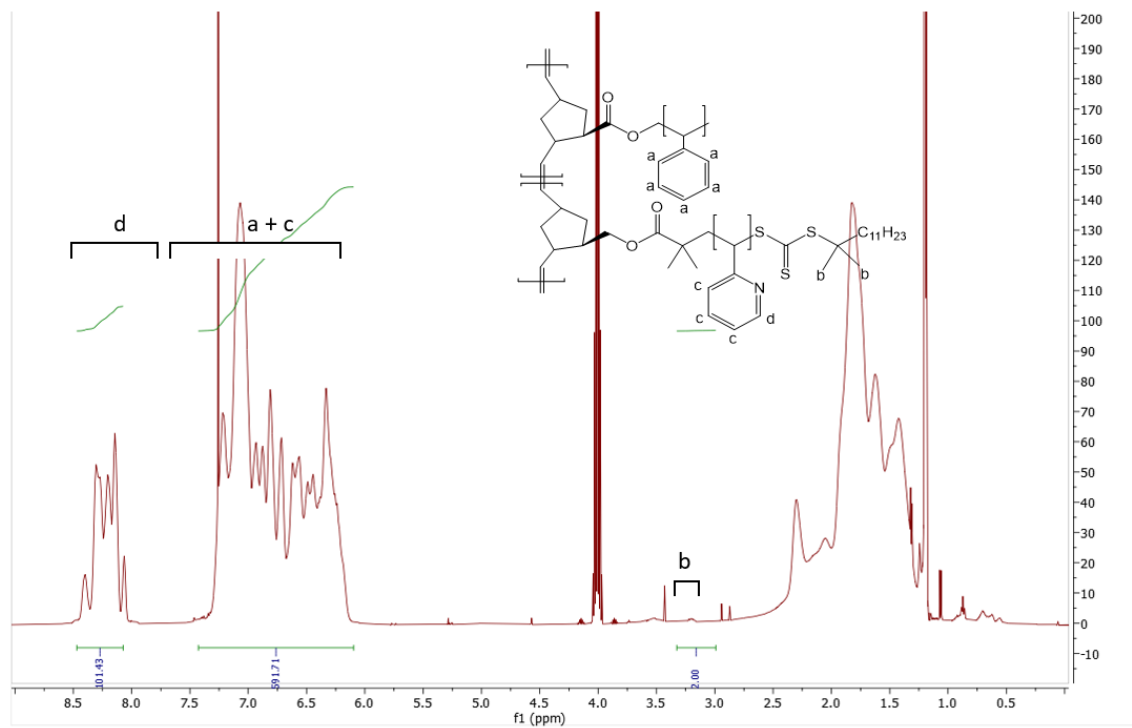


Figure B.21: NMR spectrum for BB₁₀. The protons from styrene (a, 5H, 6.25-7.3 ppm) and 2-vinylpyridine (c, 3H, 6.3-7.3 PPM; d, 1H, 7.9-8.4 ppm) were integrated relative to the protons from CTA (b, 2H, 3.25 ppm) to obtain M_n of the side chain of poly(2-vinylpyridine) and mole percent of each polymer..

B.2 Gel Permeation Chromatography (GPC)

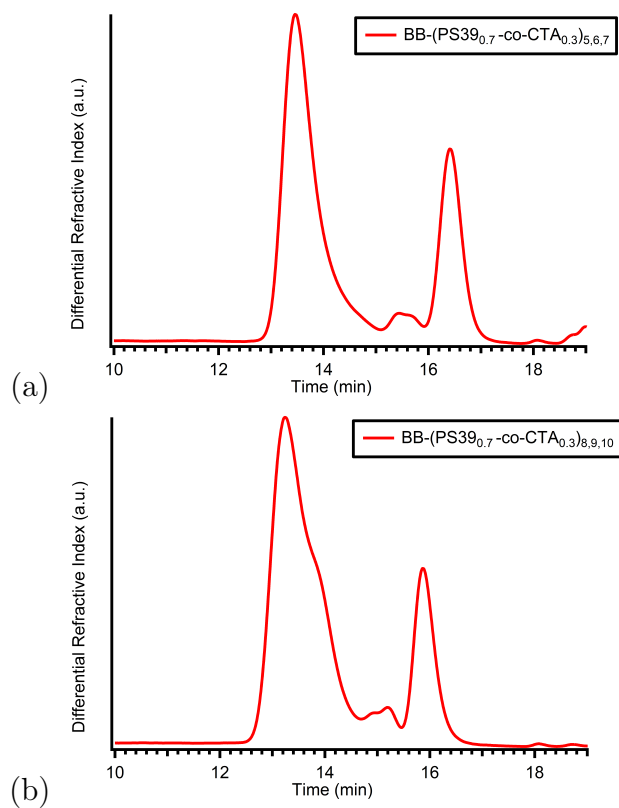


Figure B.22: GPC for precursor bottlebrush (a) B_{5,6,7} (b) B_{8,9,10}.

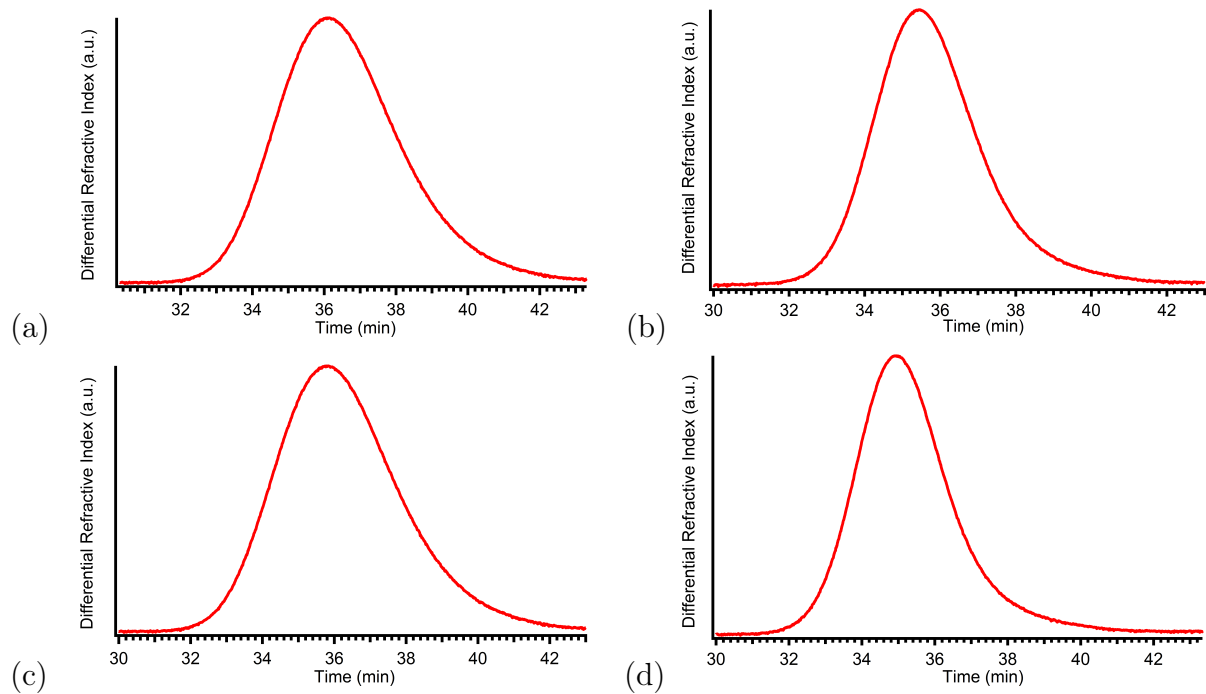


Figure B.23: GPC for (a) $P(S\text{-}co\text{-}2VP)_1$ (b). $P(S\text{-}co\text{-}2VP)_2$ (a) $P(S\text{-}co\text{-}2VP)_3$ (a) $P(S\text{-}co\text{-}2VP)_4$.

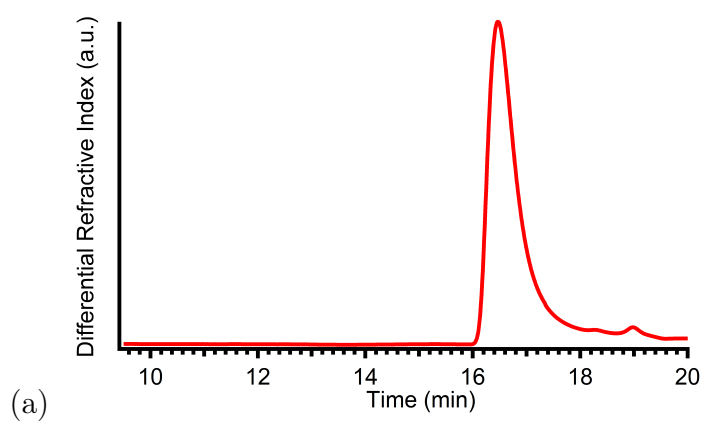


Figure B.24: GPC for $P(S\text{-}co\text{-}2VP)_5$.

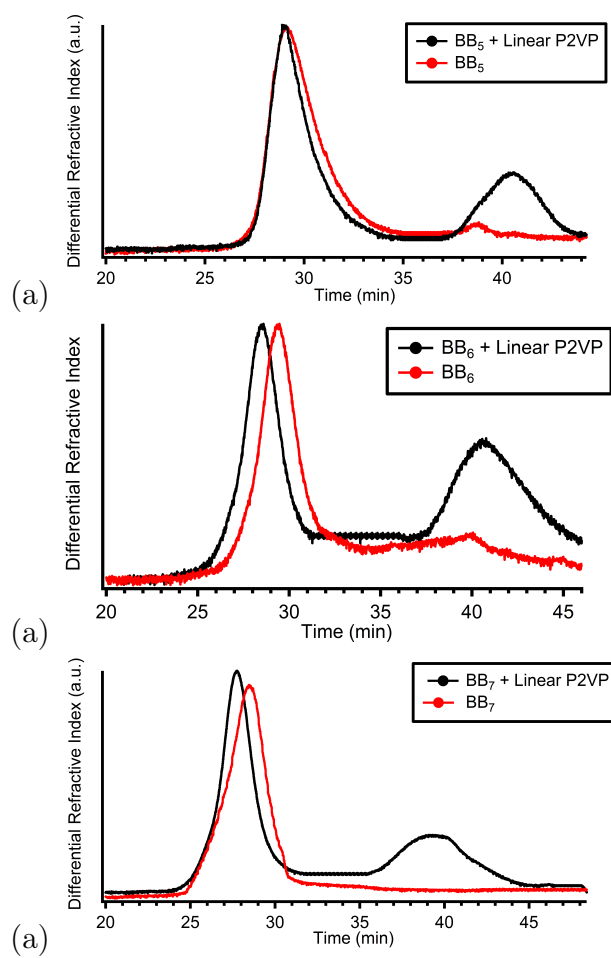


Figure B.25: GPC for (a) BB₅ (b) BB₆ (c) BB₇

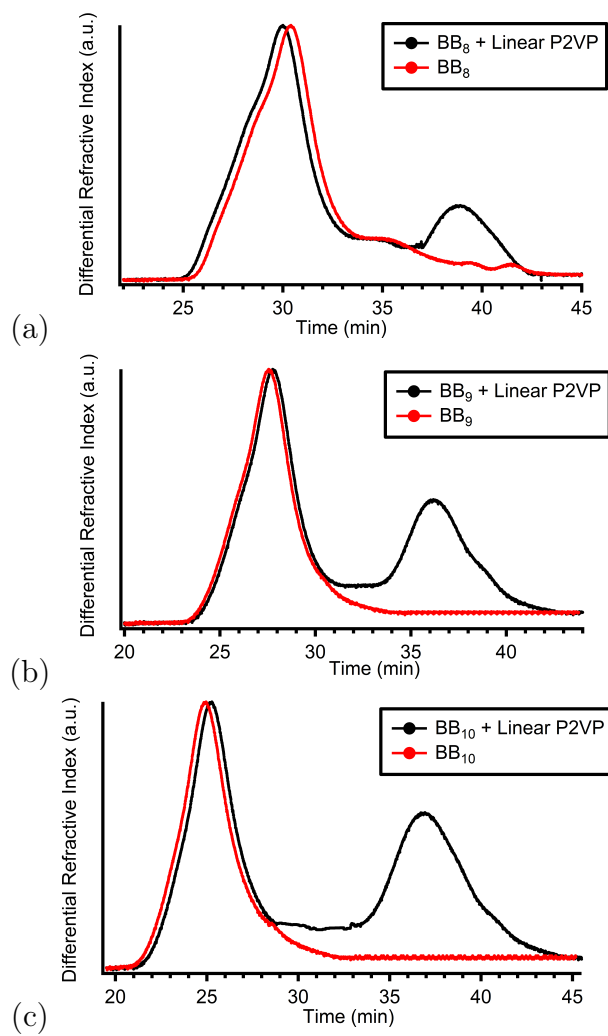


Figure B.26: GPC for (a) BB_8 (b) BB_9 (c) BB_{10}

B.3 Contact Angle Measurements

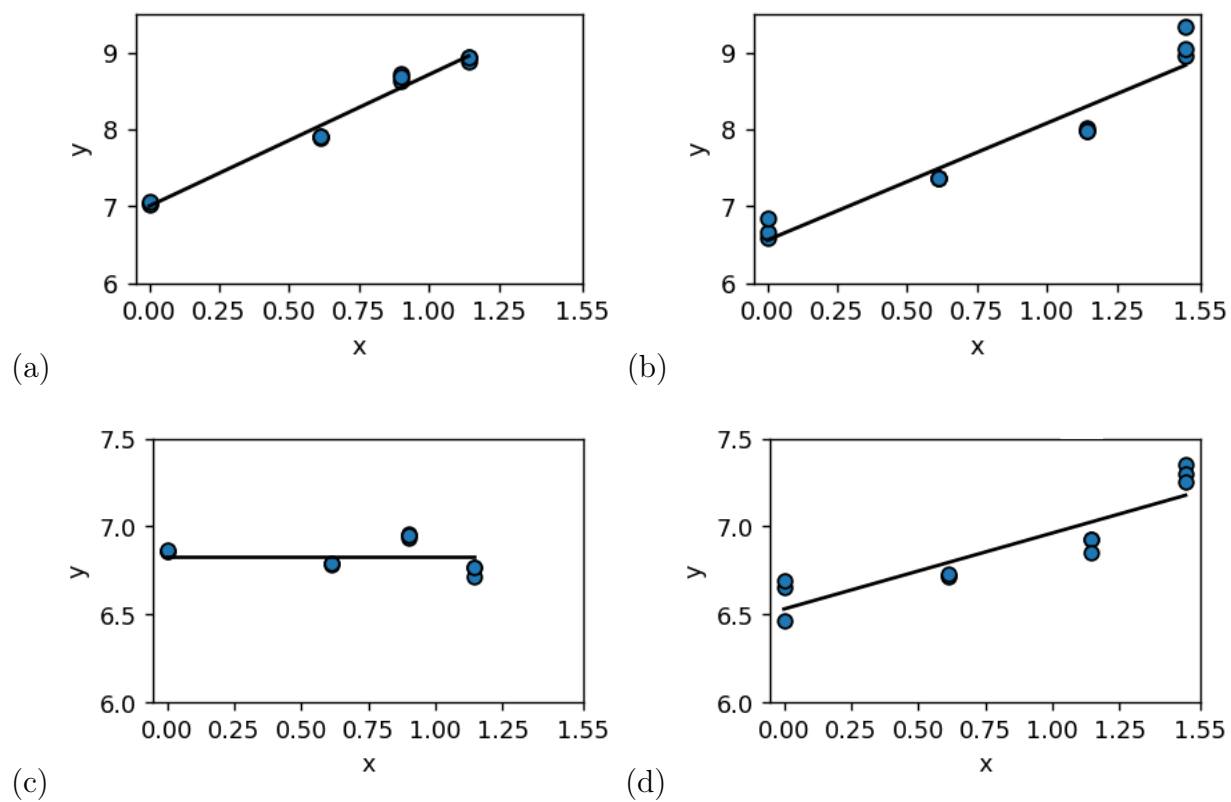


Figure B.27: OWRK fits for (a) $P(S\text{-co-}2VP)_1$ as-cast (b) $P(S\text{-co-}2VP)_1$ annealed (c) BB_{10} as-cast (d) BB_{10} annealed.

B.4 ^1H NMR for kinetic studies.

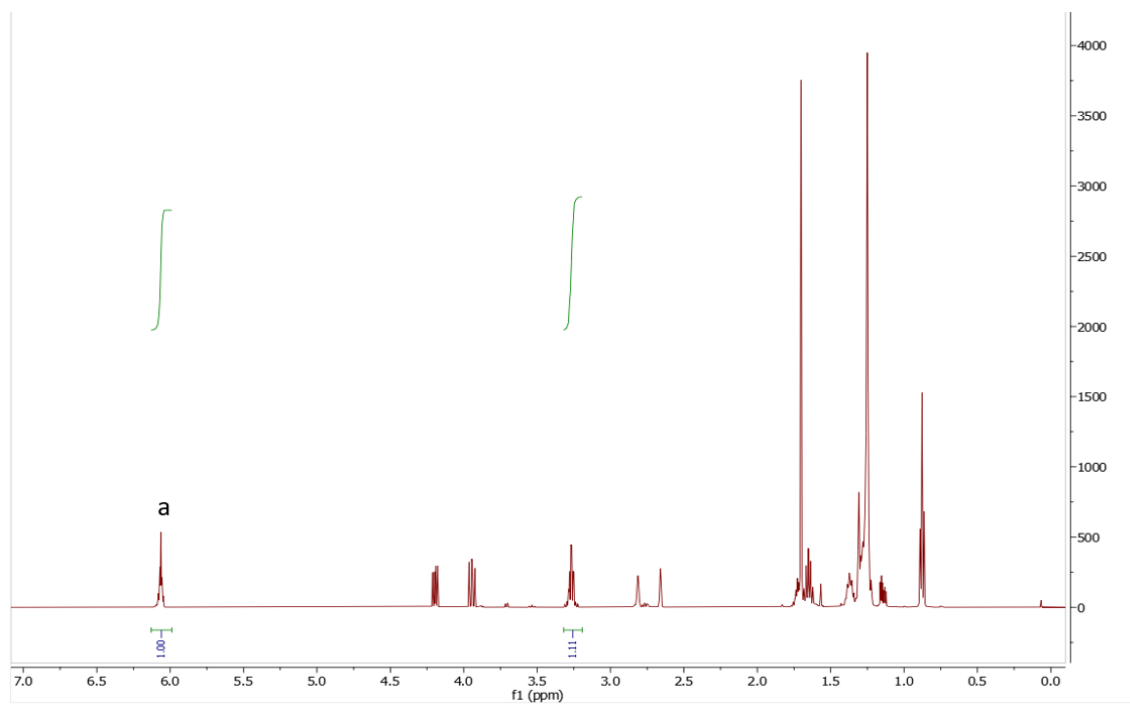


Figure B.28: NMR spectrum for NB-CTA at ($t=0$). The peak (a, 2H, 6.1 ppm) indicates presence of norbornene in NB-CTA.

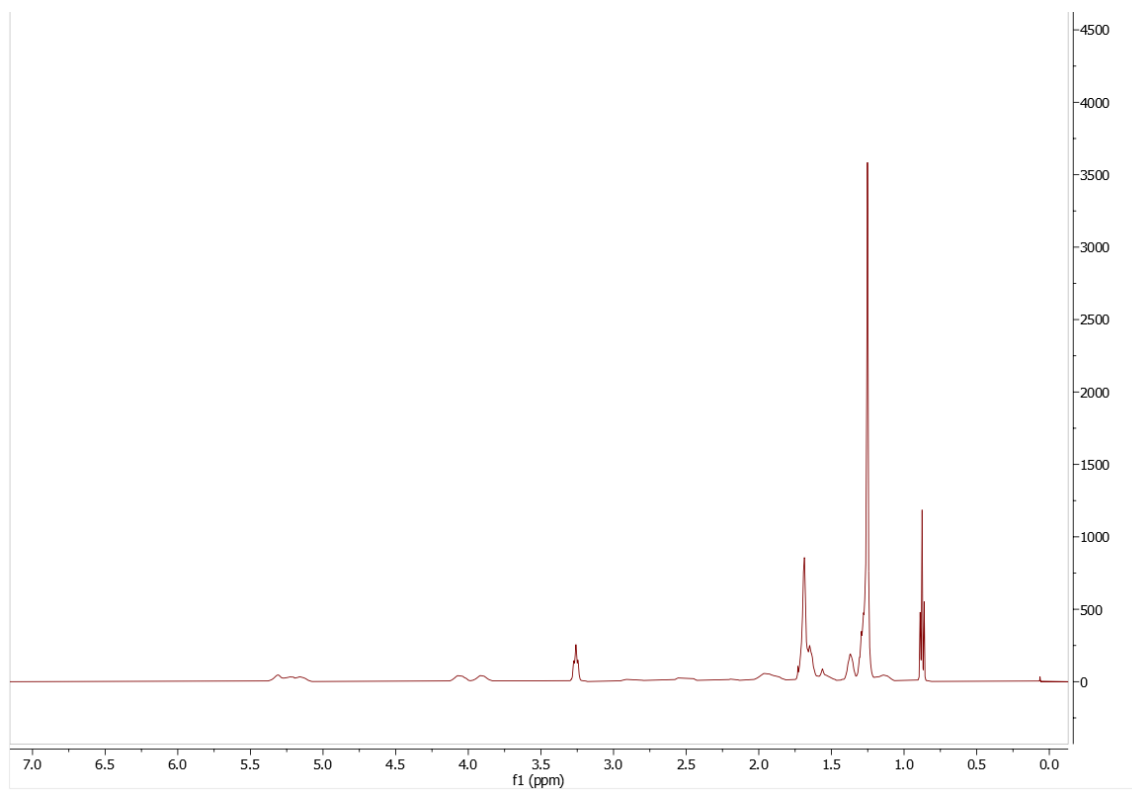


Figure B.29: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=1$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

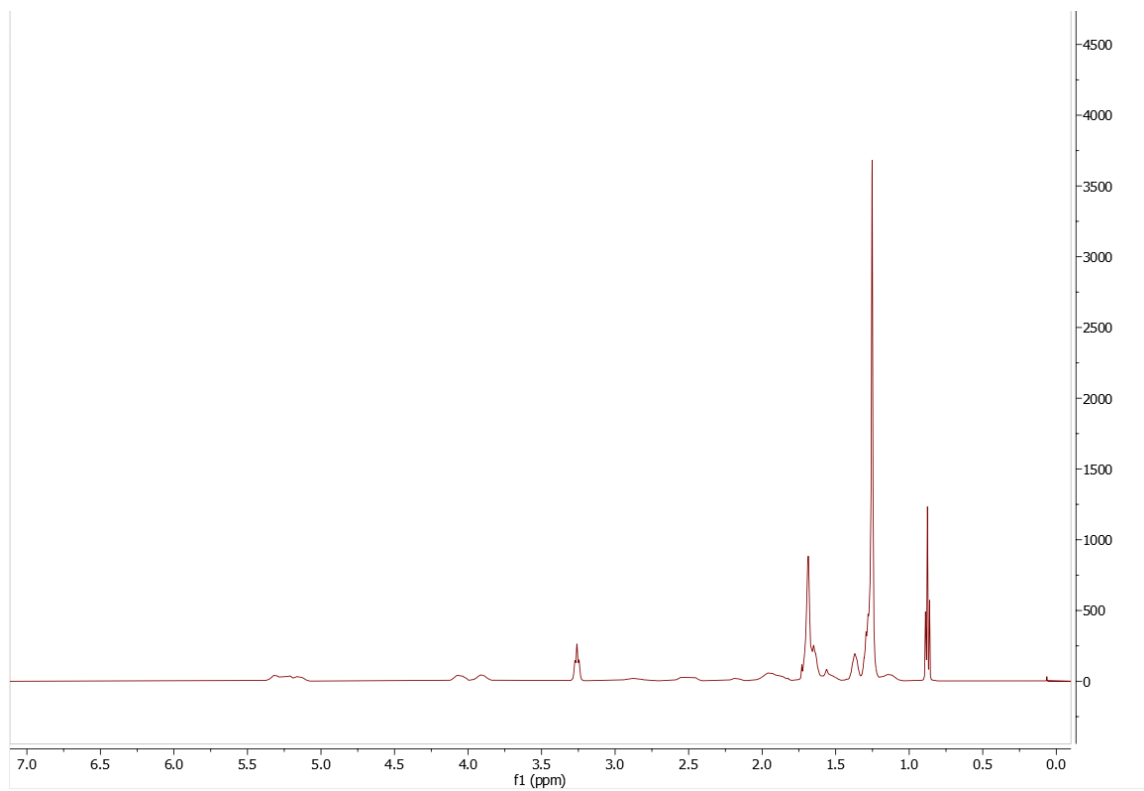


Figure B.30: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=2$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

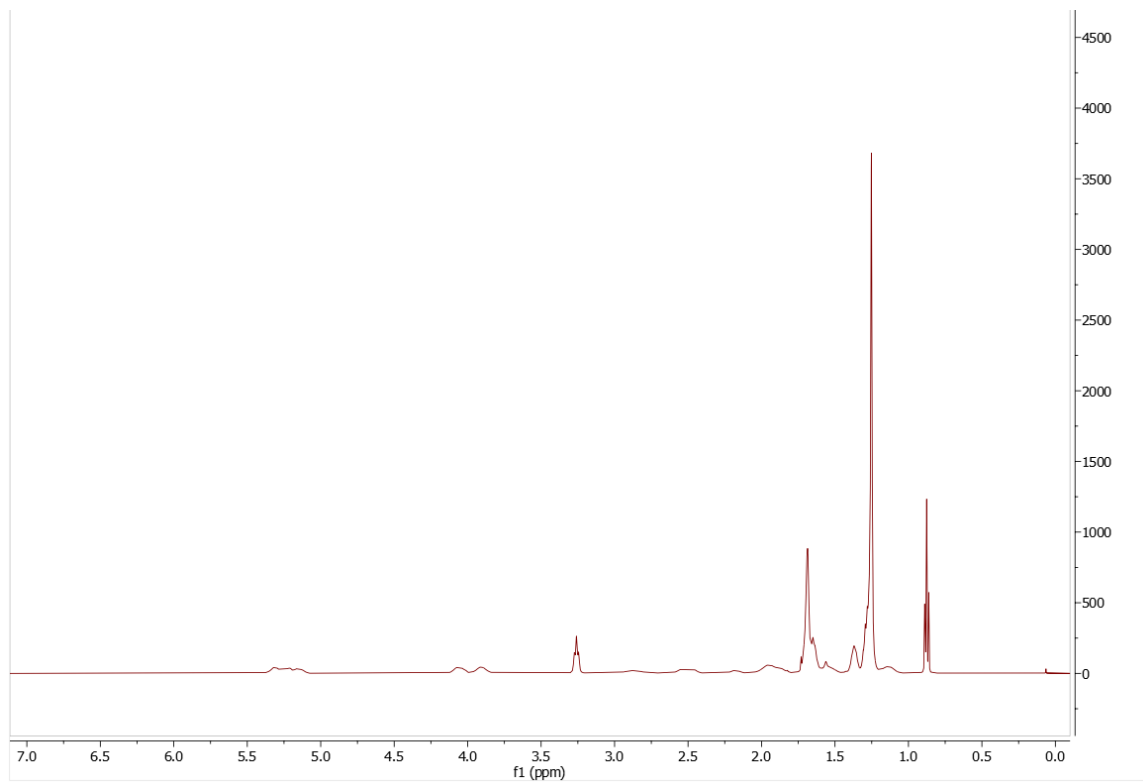


Figure B.31: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=3$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

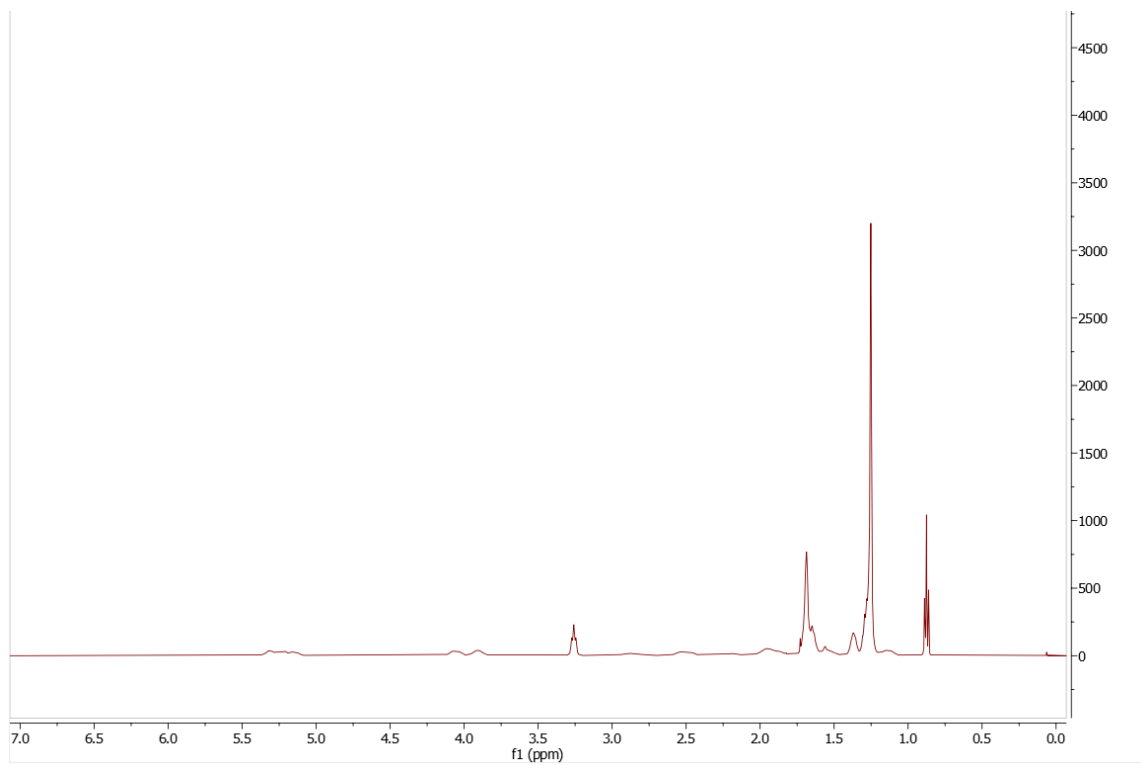


Figure B.32: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=4$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

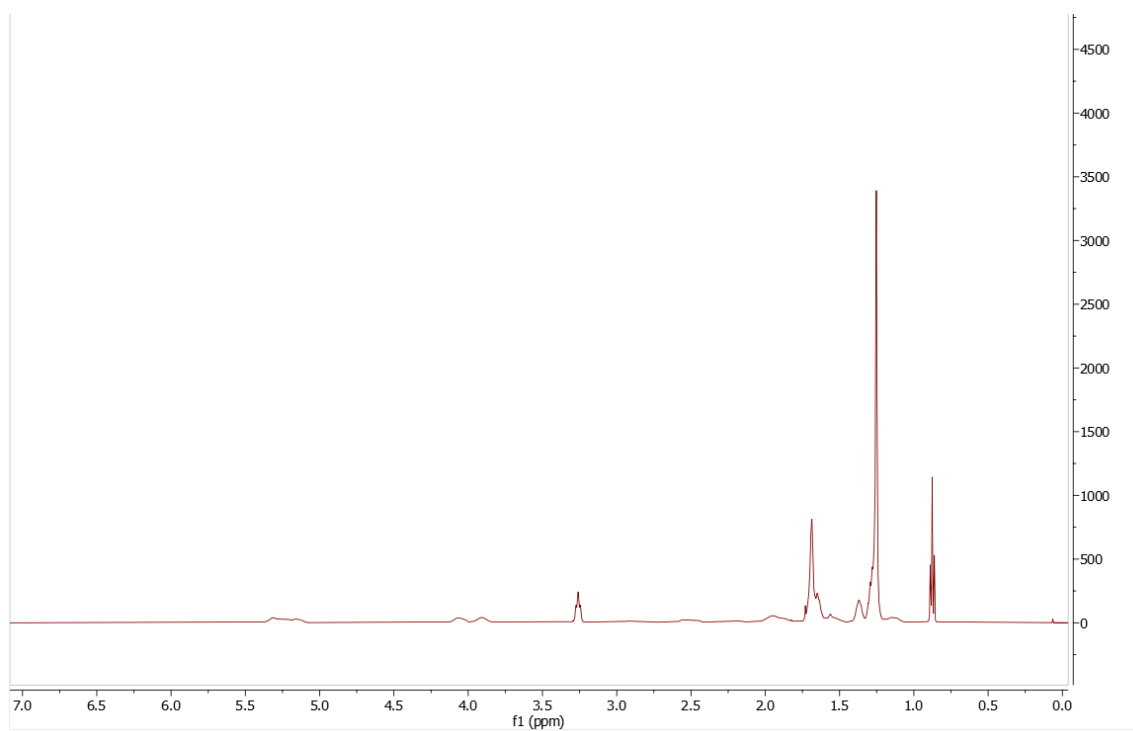


Figure B.33: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=5$). The complete disappearance of nornorbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

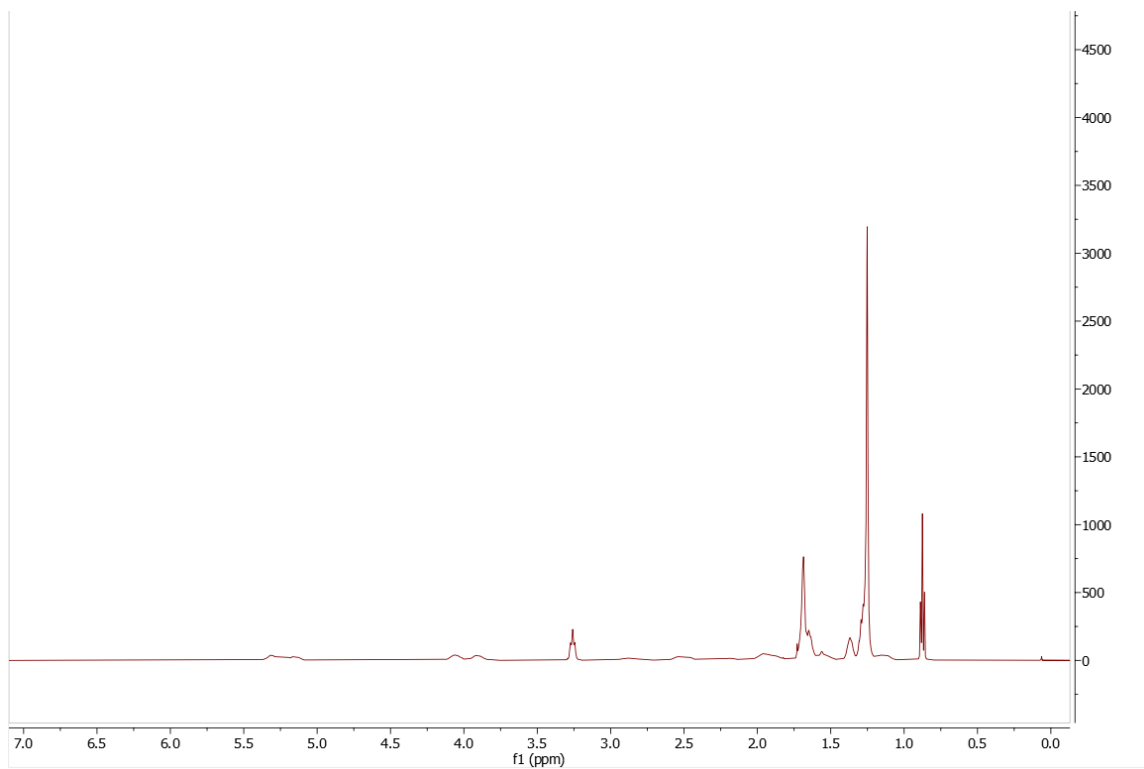


Figure B.34: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=7.5$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

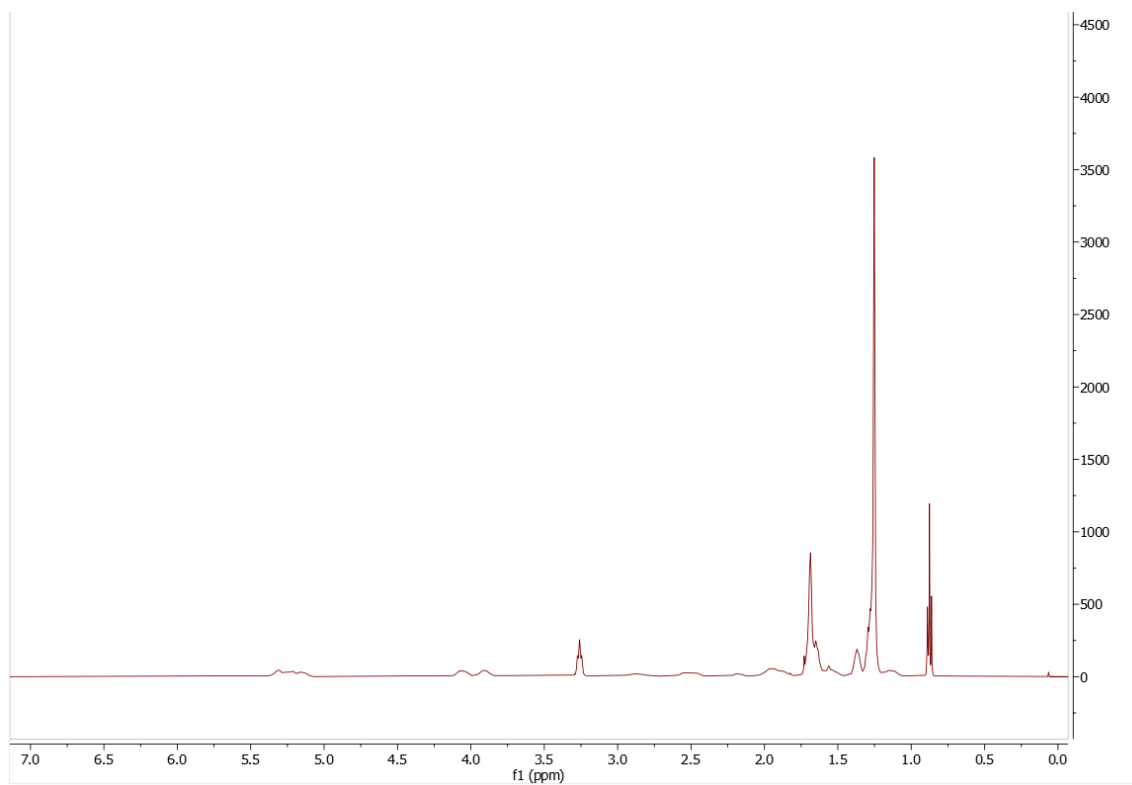


Figure B.35: NMR spectrum for homopolymerization of NB-CTA bottlebrush at ($t=10$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion of NB-CTA to bottlebrush.

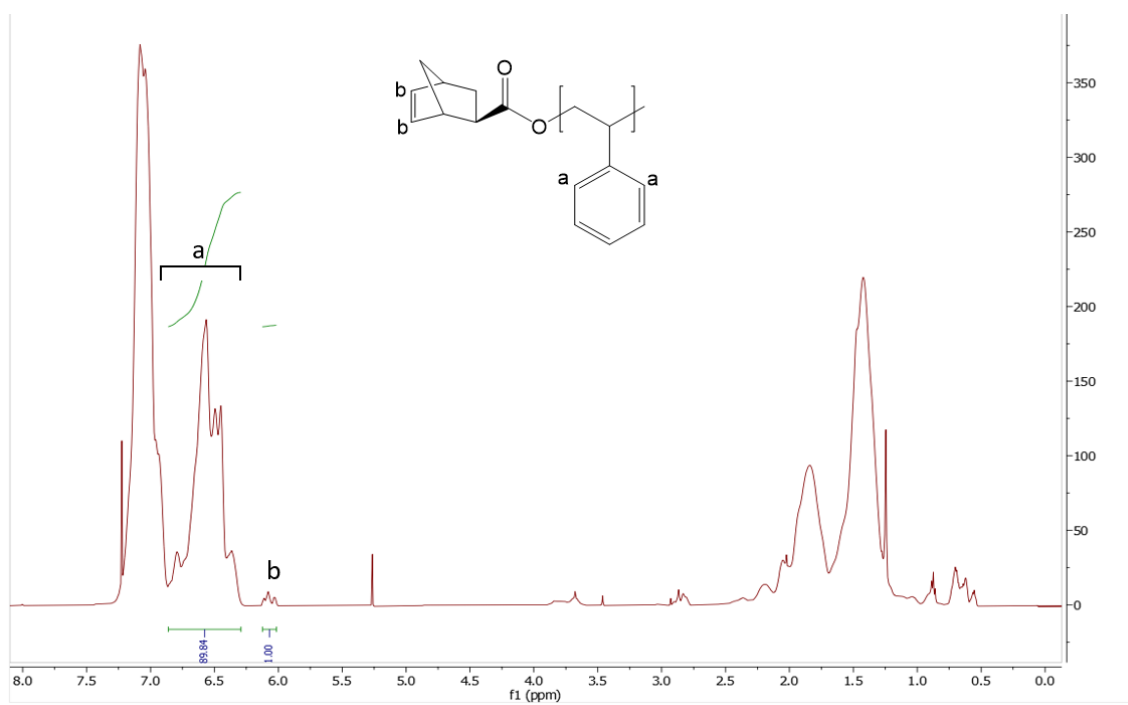


Figure B.36: NMR spectrum for NB-PS at ($t=0$). The disappearance of peak (b, 2H, 6.1 ppm) was monitored to get conversion of NB-PS macromonomer to bottlebrushes..

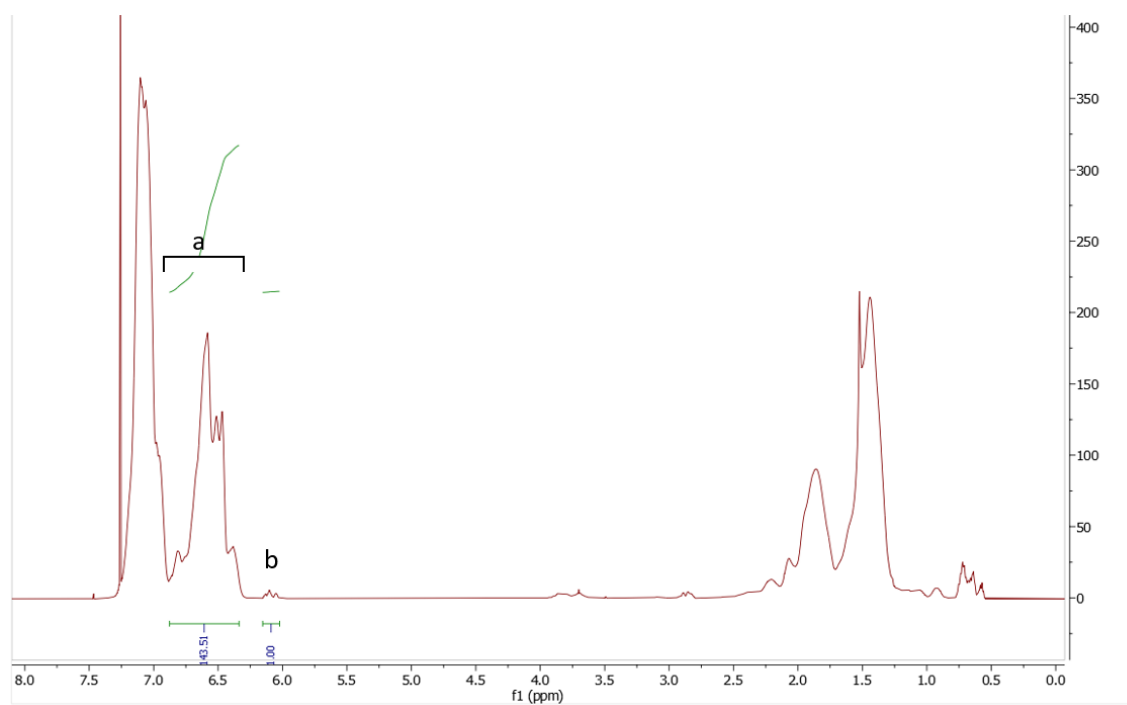


Figure B.37: NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=1). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 35% conversion of NB-PS to bottlebrush).

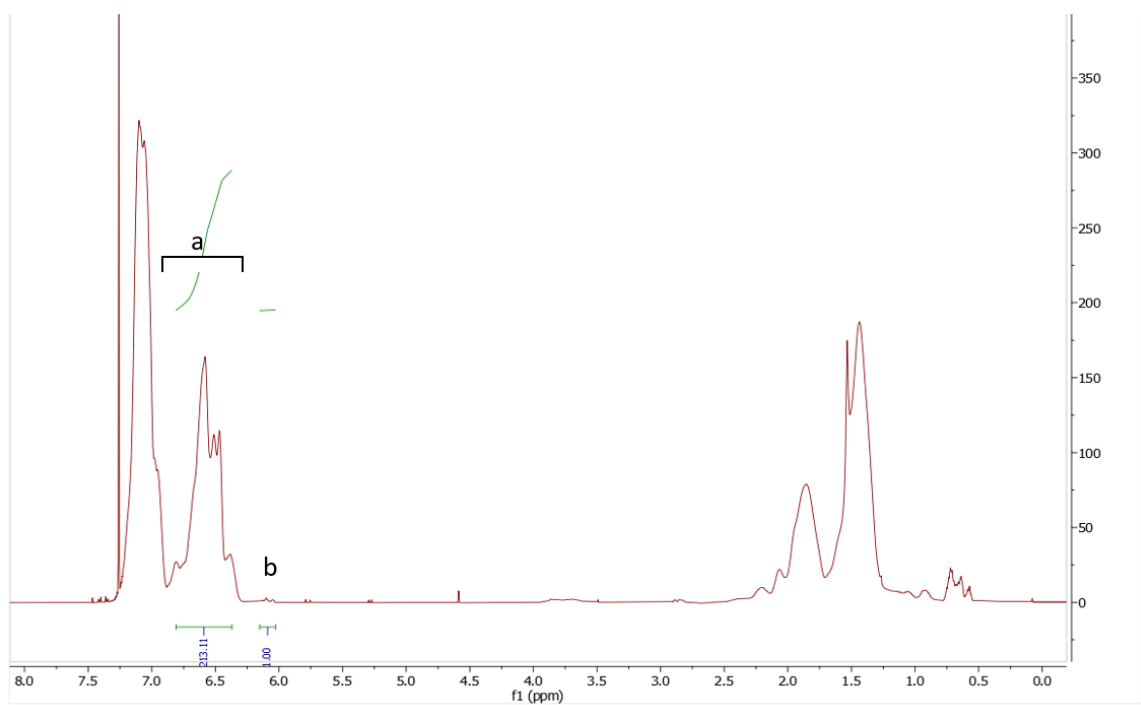


Figure B.38: NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=3). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 55% conversion of NB-PS to bottlebrush).

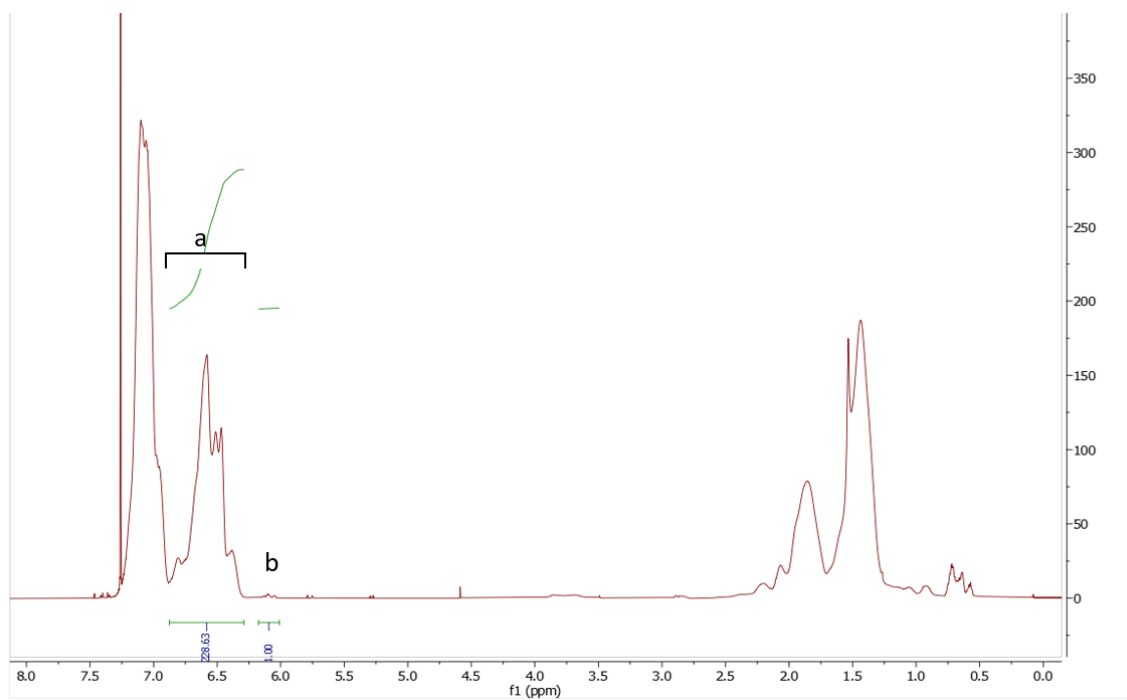


Figure B.39: NMR spectrum for homopolymerization of NB-PS bottlebrush at ($t=4$). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 60% conversion of NB-PS to bottlebrush).

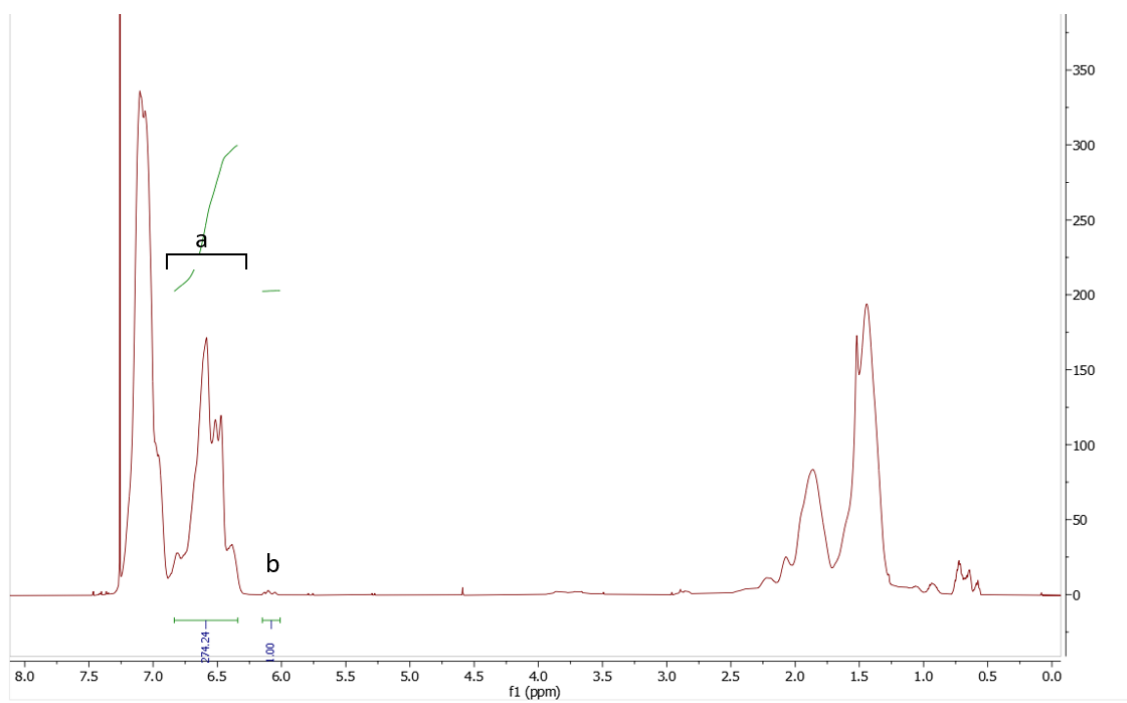


Figure B.40: NMR spectrum for homopolymerization of NB-PS bottlebrush at ($t=5$). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 71% conversion of NB-PS to bottlebrush).

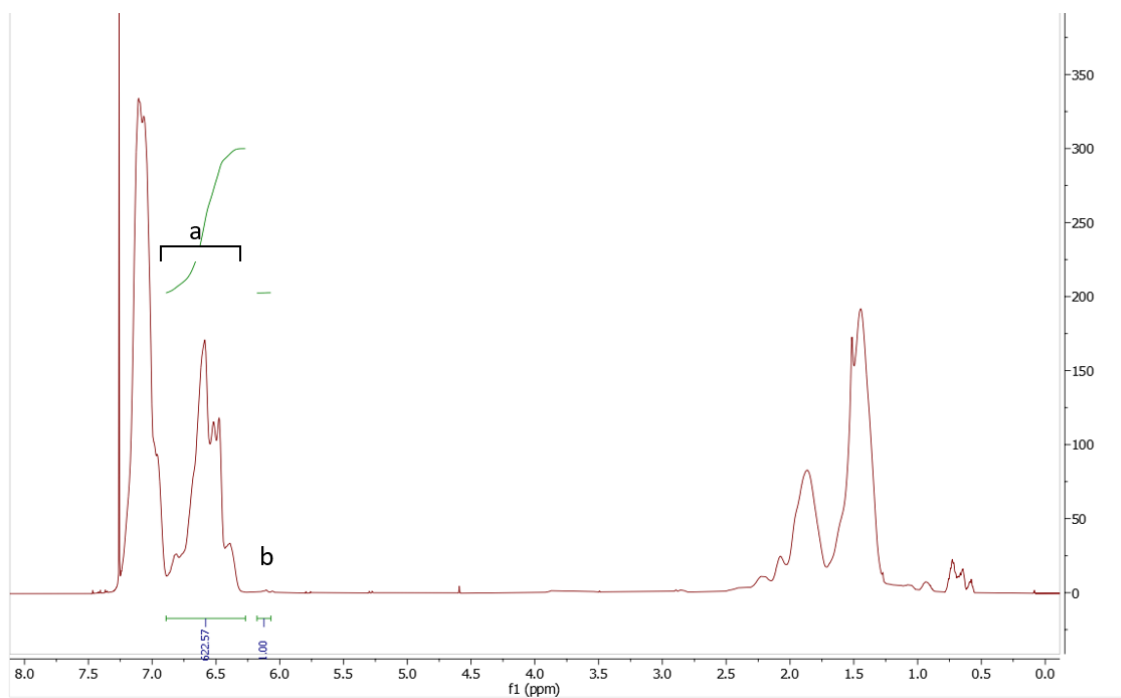


Figure B.41: NMR spectrum for homopolymerization of NB-PS bottlebrush at ($t=7.5$). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 85% conversion of NB-PS to bottlebrush).

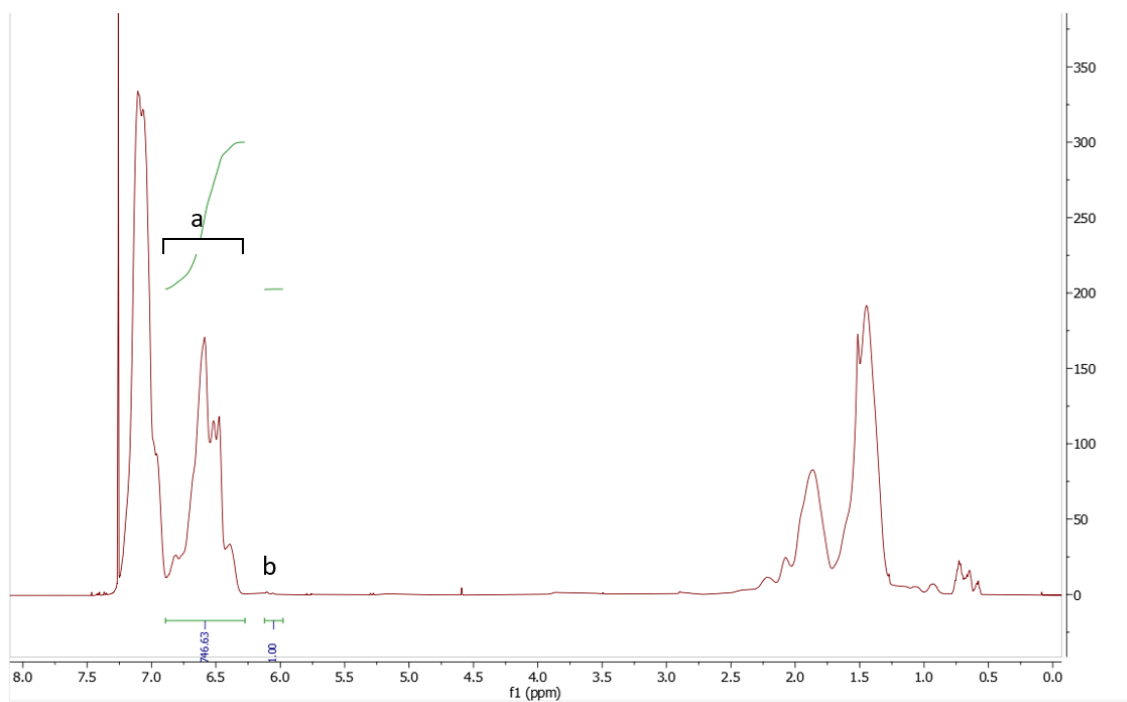


Figure B.42: NMR spectrum for homopolymerization of NB-PS bottlebrush at (t=10). The disappearing peak (a, 2H, 6.1 ppm) indicates formation of PS bottlebrushes, (approx. 89% conversion of NB-PS to bottlebrush).

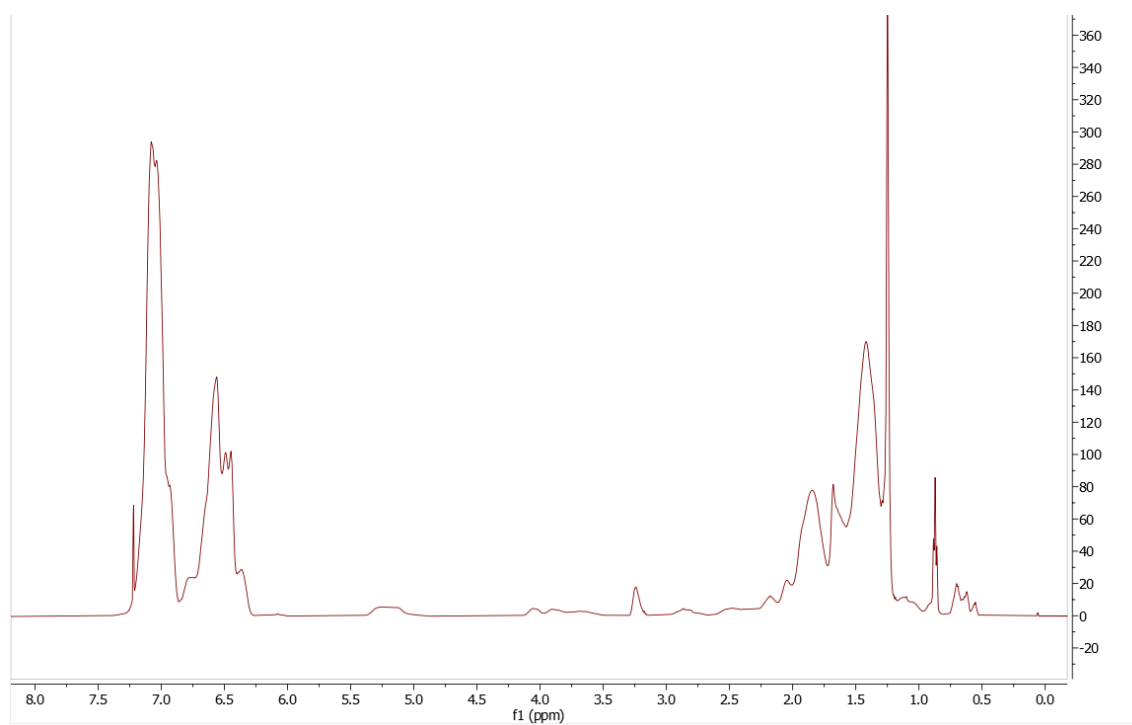


Figure B.43: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=0.5$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.

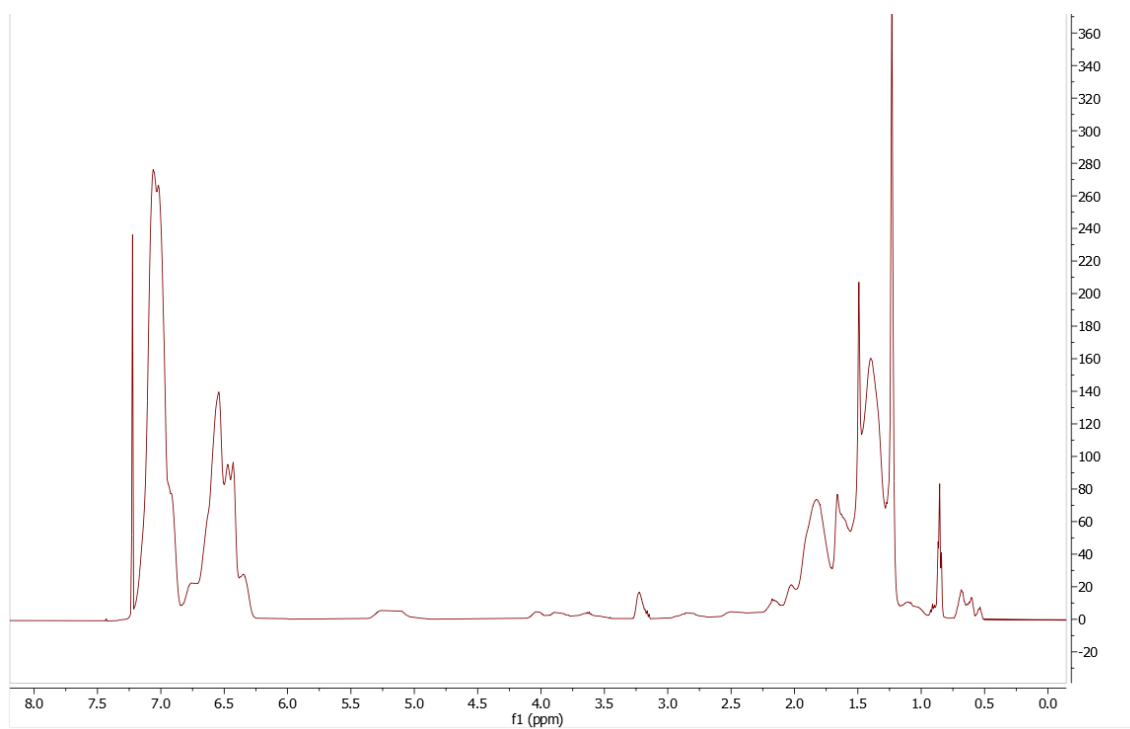


Figure B.44: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=1$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.

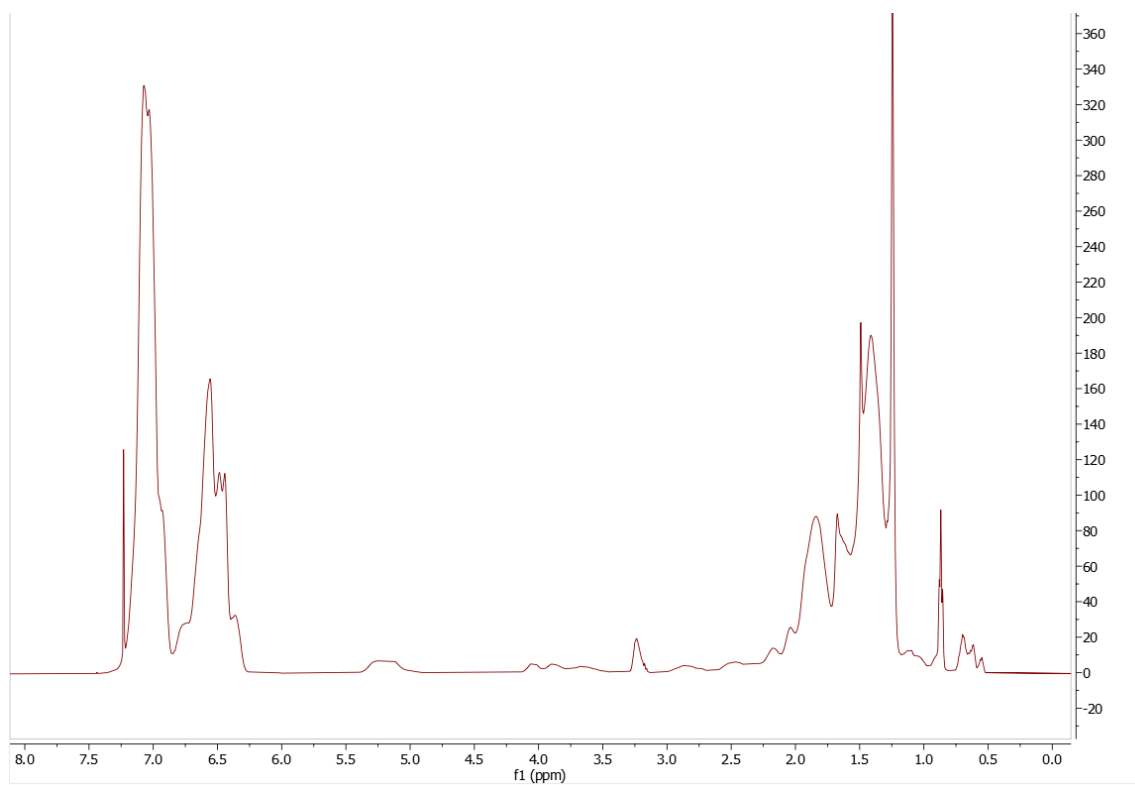


Figure B.45: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=2$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush..

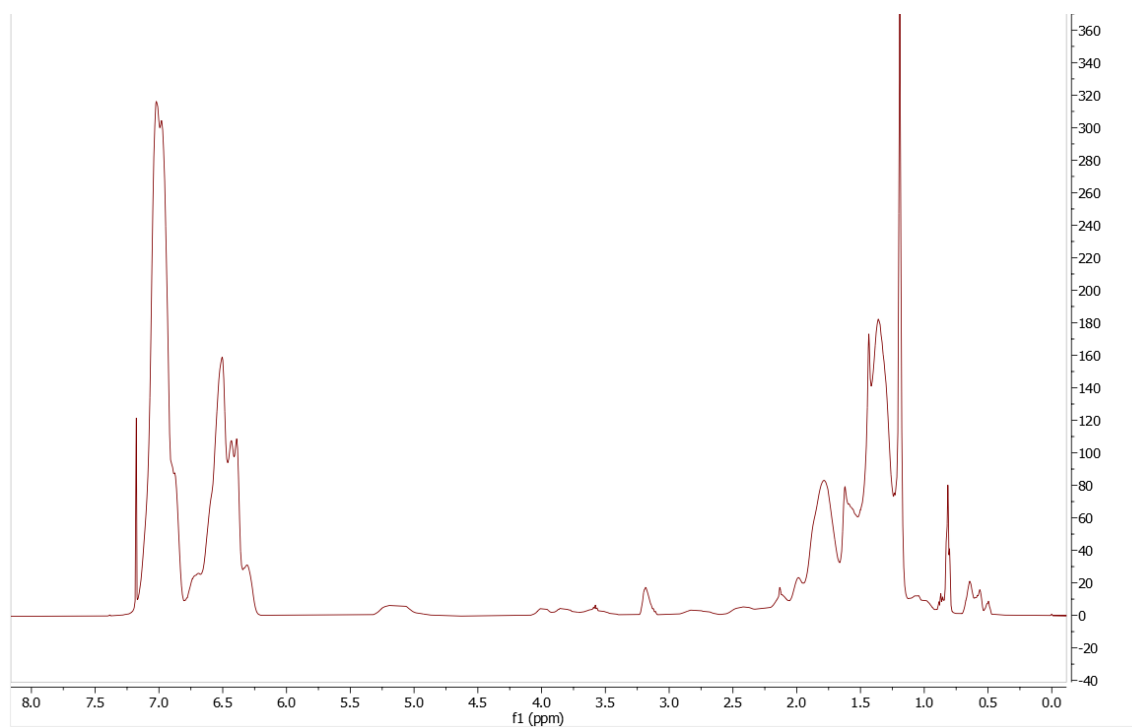


Figure B.46: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=3$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush.

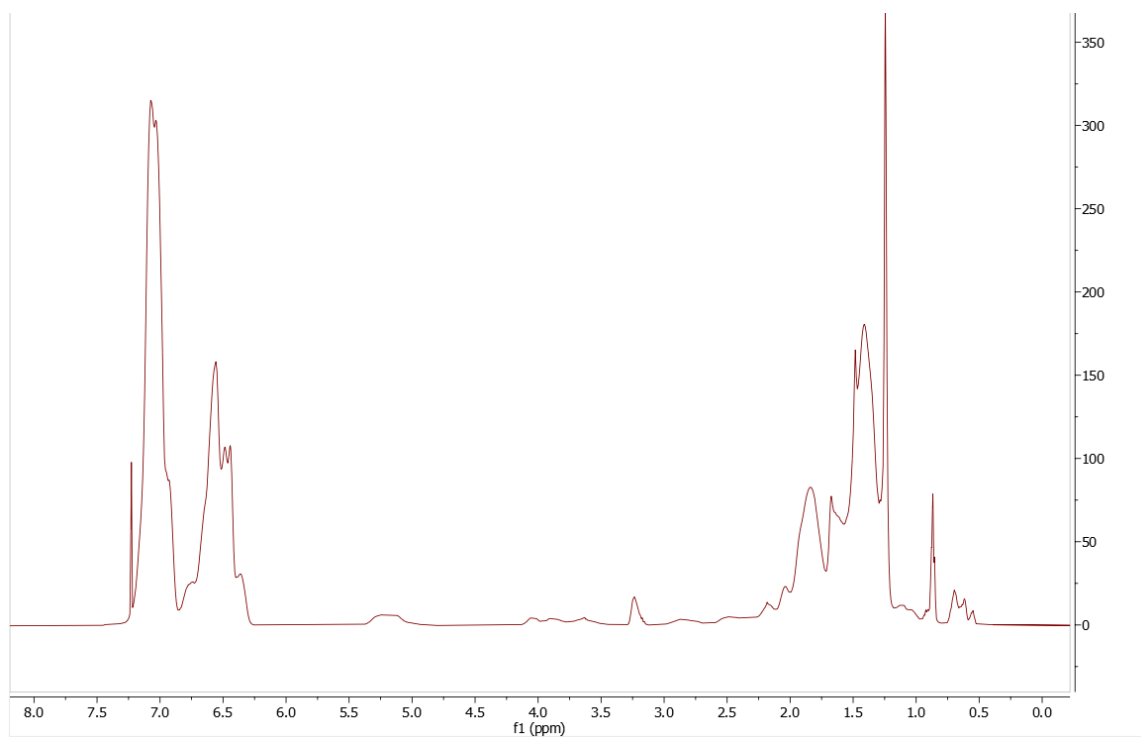


Figure B.47: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=4$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush..

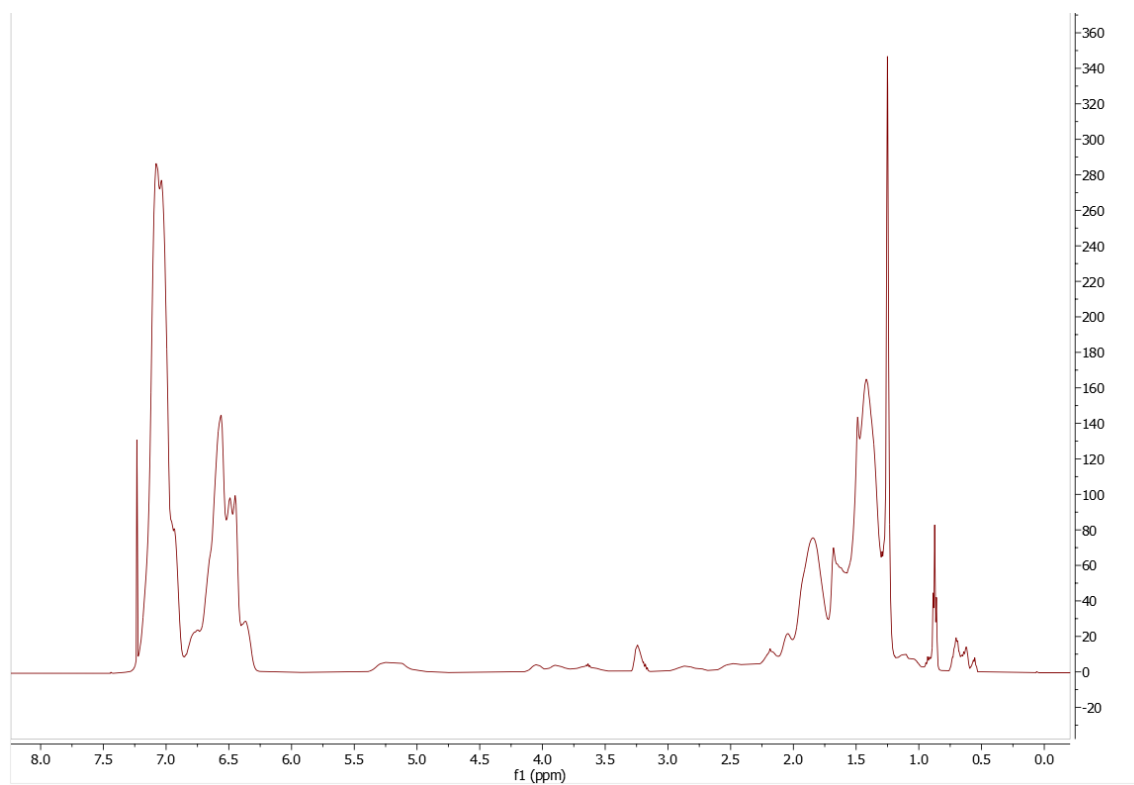


Figure B.48: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=5$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush..

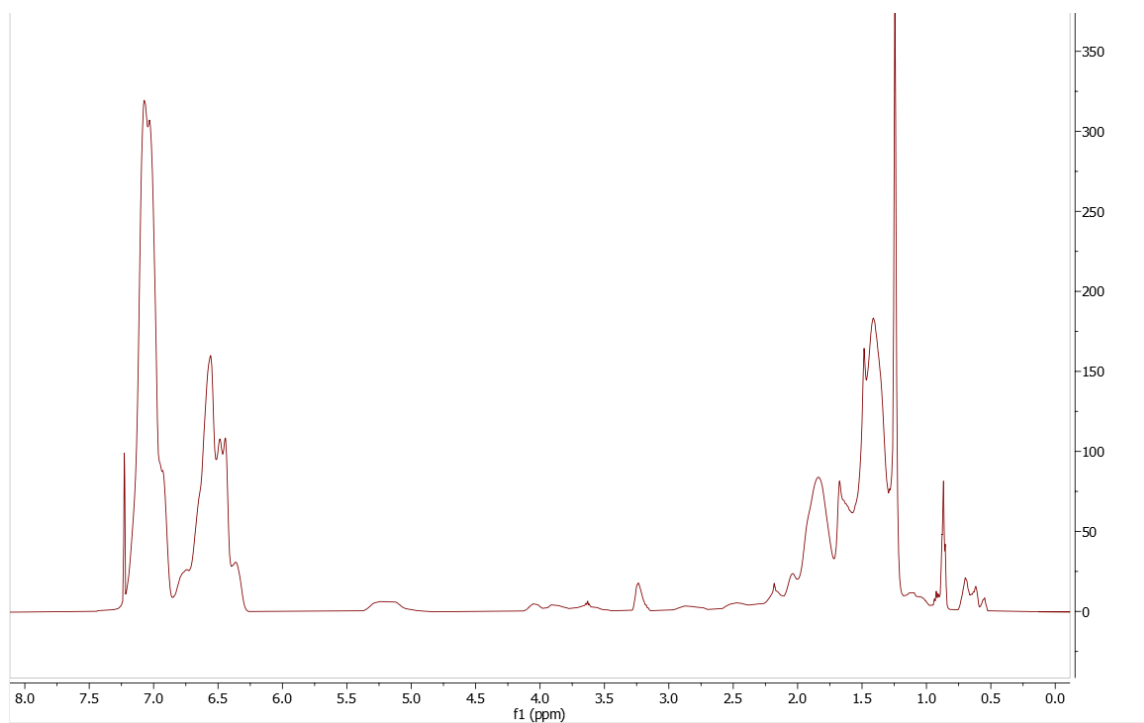


Figure B.49: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=7.5$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush..

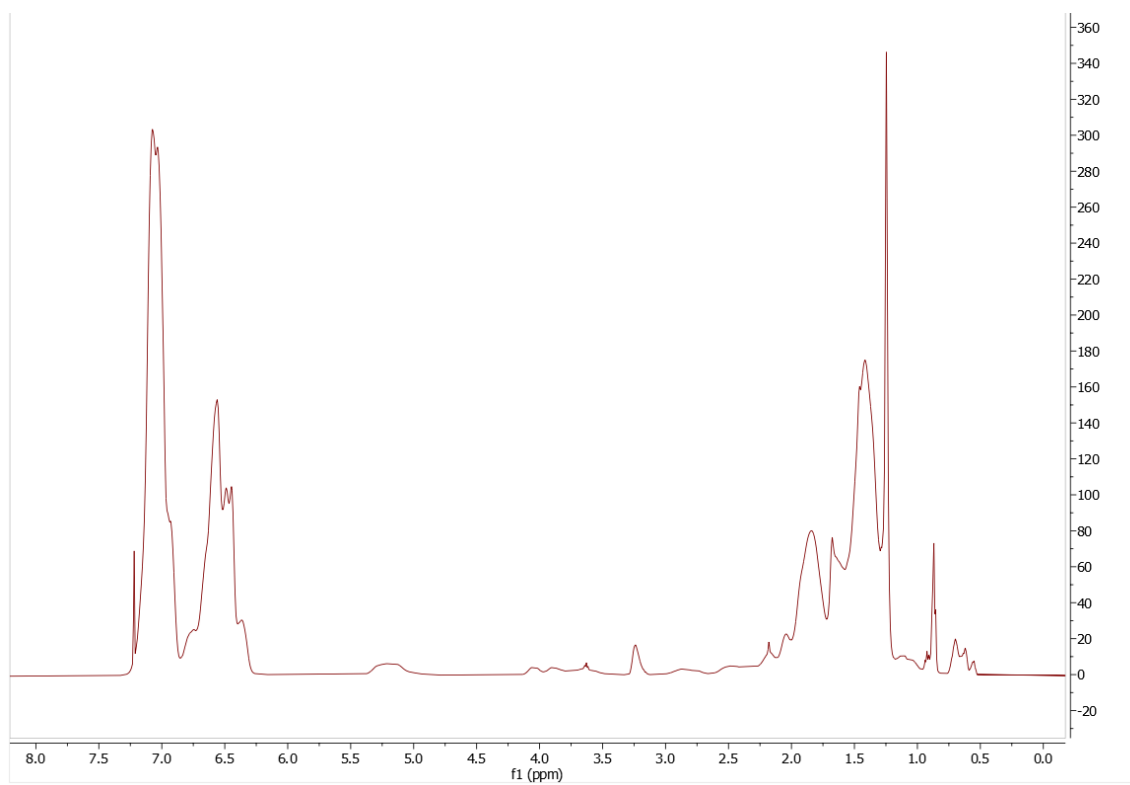


Figure B.50: NMR spectrum for copolymerization of NB-CTA and NB-PS bottlebrush at ($t=10$). The complete disappearance of norbornene peak at 6.1 ppm indicates 100% conversion to bottlebrush..

Appendix C

Calculations

Calculation of NB-CTA mol% and PS mol% in precursor bottlebrush B₁.

From Figure [A.5](#),

- Integrated area from CTA peak (b, 2H, 3.25 ppm) = 2
- Integrated area from styrene peak (a, 5H, 6.25-7.3 ppm) and (c, 5H, 6.25-7.3 ppm) = 185. This integrated area comes from precursor bottlebrush containing PS chains and unreacted PS which did not have norbornene termination. To differentiate the contributions of precursor bottlebrush and unreacted PS in the styrene peak (a + c), GPC data were used to determine the relative amounts of styrene in precursor bottlebrush and unreacted PS. For B₁, approximately 72% of the product was precursor bottlebrush and 28% of the product was unreacted PS.
- As we know the total integrated area of the styrene peak a + c = 185, but only 72% comes from precursor bottlebrush, the integrated area from the precursor bottlebrush is $185 \times 0.72 = 133$.
- To get the molar compositions of PS and NB-CTA in the precursor bottlebrush, we need to compare the integrated area coming from 1 hydrogen of PS chain and 1 hydrogen of NB-CTA chain. The integrated area for styrenic hydrogen on

the precursor bottlebrush (133) reflects all the styrene monomers in the chain, and needs to be divided by the side-chain degree of polymerization. The degree of polymerization of PS side chain is 39, Hence, the integrated area from 1 styrene unit can be obtained by dividing 133 by 39, which is 3.4. As the styrene signal arises from the 5 aromatic hydrogens, we then divide by 5 to get the contribution of 1 hydrogen, which is $3.4/5.0 = 0.68$. The integrated area from the CTA peak (b, 2H, 3.2-3.4 ppm) is 2.0, so the contribution of 1 hydrogen from the CTA is 1.0.

- Finally, the molar composition of PS side chains in the precursor bottlebrush is $0.68/(1 + 0.68) \times 100 = 40 \text{ mol\%}$.

Calculation of P2VP mol% and PS mol% in final bottlebrush BB₁. From Figure [A.7](#)

- Integrated area from CTA peak (b, 2H, 3.25 ppm) = 2
- Integrated area from 2-vinylpyridine peak (d, 1H, 7.9-8.4 ppm) = 9.38
- Integrated area from styrene and 2-vinylpyridine peak (a, 5H, 6.25-7.3 ppm) and (c, 3H, 6.25-7.4 ppm) = 127.49
- The integrated area from hydrogen next to nitrogen on 2-vinylpyridine (peak d, 1H, 8-9 ppm)) = 9.38. This contribution should be same for each hydrogen in pyridine ring. Therefore, $d = c = 9.38$.
- Peaks (a, 5H, 6.25-7.3 ppm) + (c, 3H, 6.25-7.4 ppm) come from 5 aromatic protons on styrene and 3 of the aromatic protons on 2-vinylpyridine. This can be written as: $5a + 3c = 127.49$
- $5a + (9.38 \times 3) = 127.49$
- $5a + 28.14 = 127.49$

- $5a = 99.35$
- $a = 19.87$
- $\text{mol\% P2VP in the final bottlebrush} = d/(a + d) \times 100 = 32\%$
- $\text{mol\% PS in the final bottlebrush} = a/(a + d) \times 100 = 68\%$

Calculation of backbone degree of polymerization (N_b) for bottlebrush copolymers B_1

- M_n for NB-PS side chain = 4,500 g/mol
- M_n for NB-CTA = 470.81 g/mol
- Percentage side chains of NB-PS in precursor bottlebrush copolymers = 40%
- Percentage side chains of NB-CTA in precursor bottlebrush copolymers = 60%
- M_w of precursor bottlebrush copolymers B_1 from GPC = 209,000 g/mol
- Weight average M_n for side chains = $(4,500 \times 0.4 + 470.81 \times 0.6) = 2,082$ g/mol
- Degree of polymerization of precursor bottlebrush $B_1 = 209,000/2082 = 100$

Products

Publications

1. **Charpota, N.**, Terlier, T., Verduzco, R., Stein, G. E. "Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers" (In Revision).
2. **Charpota, N.**, Brady, L., Stein, G. E. "Surface Properties of Thin Films of Bottlebrush Statistical Copolymers" (In Preparation).
3. Lee, D., **Charpota, N.**, Mei, H., Terlier, T., Pietrzak, D., Stein, G.E., Verduzco, R., "Impact of processing effects on surface segregation of bottlebrush polymer additives," *Macromolecules*, 55, 8909-8917, 2022.

*Equal Contribution

Presentations

1. **Charpota, N.**, Terlier, T., Verduzco, R., Stein, G. E. "Wetting Reversal in Blends of Bottlebrush Copolymers and Linear Homopolymers". American Physical Society March Meeting 2024: Oral.
2. **Charpota, N.**, Laws, T., Verduzco, R., Stein, G. E. "Design rules for bottlebrush copolymers as surface-active additives for commodity homopolymers". American Chemical Society 2022: DPOLY Poster.

Vita

Nilesh grew up in Banswara, a small town in Rajasthan, India. After his high school graduation, he qualified for the prestigious IIT-JEE examination and earned his Bachelor of Technology in Chemical Engineering from Indian Institute of Technology, Hyderabad. During his Bachelor's, he worked as an undergraduate researcher under Dr. Chandra Shekhar Sharma studying electrospun nanofibers. After taking a gap year preparing for the GRE and TOEFL, he went to the University of Florida in the United States and earned his Master of Science in Chemical Engineering, where he worked as a research assistant under Dr. Peng Jiang studying shape memory polymers with tunable wettability. He then moved to Knoxville, Tennessee, where he started his PhD under Dr. Gila Stein at the University of Tennessee. After graduation, he plans to continue his career in an industry setting.