Nanostructured Self-assembled Thin Films of Cationic Bottlebrush Block Copolymers

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NANOSTRUCTURED SELF-ASSEMBLED THIN FILMS OF CATIONIC BOTTLEBRUSH BLOCK COPOLYMERS

By

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A DISSERTATION

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Biofouling which is an accumulation of small species on submerged surfaces that causes detrimental impacts on economic and environmental factors for aquaculture activities and human health. To suppress the fouling, polymeric coatings from amphiphilic block copolymers provide nanostructured surfaces and carry multiple functional groups in a molecular chain. Polymers with quaternary ammonium functional groups enable material coatings to inhibit microbial adhesion by killing bacteria, consequently prolonging the material efficiency of, for example, medical implanted devices. Herein, well-defined architectures with full-arm density of quaternary ammonium bottlebrush polymers were generated from grafting-through ring opening metathesis polymerization (ROMP). Factors such as the halide counter ions, the molecular weight of MMs, and the pendent alkyl groups were scrutinized to understand how they affected ROMP kinetics. As a result, halide-ligand exchange between halide counter ions and Grubbs catalyst occurred and the polymerization deviated from pseudo first-order kinetics, but still followed controlled polymerization with desired molecular weight and dispersity below 1.30. Larger MMs and pendent alkyl groups reduced the ROMP propagation rates due to steric hindrance between the growing chains and incoming MMs. Next, a library of amphiphilic BBCPs were synthesized by
sequential polymerization of polystyrene MMs (PS) and quaternary ammonium MMs to afford controlled macromolecular brush copolymers. To study phase separated morphologies of thin films corresponding to each block composition analyzed by atomic force microscopy (AFM), the desired BBCPs had volume fraction of PS and cationic domain as 25:75 and 50:50, respectively. As a result, AFM images showed morphological changes corresponding to different block compositions and side chain length symmetry. Additionally, morphology stability was investigated upon water submersion. The polymer films with 50:50 volume fraction demonstrated the morphology stability after water submersion for 3 days. The results of phase separated morphologies of the BBCP films are beneficial to create a promising amphiphilic coating that possess antimicrobial absorption on the surfaces. However, the study of antimicrobial performance of the BBCP thin films has not conducted yet.
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CHAPTER 1

BIOFOULING

1. Introduction

1.1 Biofouling in marine aquaculture

Biofouling is the undesirable accumulation of small species on material surfaces submerged under a wet environment. Biofouling takes place in various applications and is commonly observed in aquaculture industries and activities.\(^1\) Marine fouling is the unwanted settlement of marine organisms such as barnacles, diatoms, algae, or tubeworms.\(^6\) It causes heavy weight on cages and fishing nets, consequently leading to material deformation and a blockage of nutrient exchange between the surfaces (Figure 1.1A). Fouled nets in farm production impede the water exchange that can bring oxygen in and remove the waste out of the farm. The poor water circulation can reduce the quality of water by lowering the amount of dissolved oxygen, consequently negatively impacting fish growth.\(^2\) Species growth in pipelines used for industrial cooling systems generates potential clogging, drastically reducing the heat exchange efficiency of a generator.\(^3\) Fouling on a ship hull increases frictional resistance from increased surface roughness and deteriorated surfaces, which causes higher fuel consumption and greenhouse gas generation during a voyage (Figure 1.1B). Additionally, fouling animals on the moving ship hull can migrate to other locations in the sea in which they do not naturally exist which, can interfere with the life cycle of the local species.\(^4\) Hence, the fouled surfaces in aquaculture activities are practically eliminated by physically cleaning or replacing with new materials. For example, the fouling on the ship hull can be removed by the dry-docking method which requires long cleaning processes and costly maintenance.\(^5\) The fouled net need cleaning periodically since the fouling can occur after the cleaned nets are put back under water again. The multiple cleaning of the fouled nets can cause stress to the animals, thereby affecting farm productivity.\(^2\)
Figure 1.1. Marine fouling on material surfaces used under sea water. A) fishing nets, and B) the hull of a ship.¹

Marine fouling growth on bare material surfaces occurs through several key steps, starting with the rapid and reversible step of conditioning film formation through the physical absorption of biomacromolecules such as proteins, polysaccharides, and glycoproteins on surfaces. Then, bacteria approach the conditioning film to gradually attach by secreting a biofilm extracellular matrix that acts as a nutrient source for permanent colonization. Next, micro-scale species, such as diatoms, larva, or microalgae grow and then favor macro-scale colonization of barnacles and others to complete their life cycle as a permanent settlement (Figure 1.2).⁵ To address the unwanted growth of marine species on the surface, the reversible formation of the conditioning layer needs to be prevented.

Figure 1.2. Schematic marine-fouling process starting from a reversible conditioning film forming to an irreversible settlement.⁶
1.2 Biofouling in medical fields

Biofouling is closely associated with serious life-threatening, healthcare-associated infections when it occurs in implanted medical equipment. The insertion of synthetic devices into the body to replace or restore some essential functions such as catheters, fracture fixation devices, and endotracheal tubes is an indispensable strategy. However, the insertion of human-made materials could lead to detrimental consequences since they are colonized by bacteria, likely causing infection (Figure 1.3A – 1.3B). In 2011, the National Healthcare Safety Network of the Centers for Disease Control and Prevention (CDC) reported that there were approximately 722000 hospitalized cases in the USA that resulted from infections, and one-fourth of those were directly associated with implanted medical devices.\(^7\) Catheters are the most common devices to be used in clinical treatment. Central venous catheter (CVC) failure-associated bloodstream infection has a 12-25% mortality rate and the annual expenses from such medical treatment are estimated up to 2.3 billion dollars a year.\(^8,9\) Urinary catheter-associated devices are extensively infected despite a low mortality rate below 5%.\(^10\) Interestingly, the numbers of the implanted materials utilized to treat urinary-associated issues were 6 times as same as that of CVC-based devices.\(^10\) So, urinary catheter-associated infections resulting in bloodstream infections were one of the leading causes of hospitalized cases. More importantly, medical inserted devices, used as replacing or restoring materials to maintain the proper functioning in the body, have encompassed a large body of devices (Figure 1.3C).\(^15\) Once the inflammation triggers, the clinically conventional technique is to use antibiotic medicines to heal the illness. Unfortunately, antibiotics usage tends to be ineffective after the microbial colonization fully takes place on surfaces.\(^11,14\) Thus, the unavoidable technique is the removal of the infected implant for a new replacement,\(^12\) which is costly and is detrimental to the patient’s health. However, the reinserted devices are still likely to get infected inside the patient’s body again. The multiple surgeries for implantation can
reduce life quality and life span of the patient. In other words, the operation after infections is risky, costly, temporary, and undesirable. Thus, intrinsic anti-microbial materials have been attractive for scientists to explore and develop to address these shortcomings.

Figure 1.3. SEM images exhibiting biofilms on medical implants that can lead to surgical treatment for fouled device removal. A) Needleless connector, and B) pacemaker wire taken out from the infected patient. C) Common polymer-coated medical devices used for medical implantation: a) endotracheal tubes, b) peritoneal catheters, c) urinary catheters, d) fracture fixation devices with polymer-based pins, and e) central venous catheters.

Bacteria settlement begins with the weak interactions of van der Waals or electrostatic forces between the submerged device surfaces and a conditioning layer, which forms from biomacromolecule accumulation such as proteins or polysaccharides. The conditioning film formation takes place rapidly after the device surfaces are exposed to physiological fluids with surrounding factors such as temperature and pH influencing the types of colonies. Then, the corresponding bacteria come into contact with the conditioning layer to proliferate into microcolonies, referred to as a biofilm consisting of extracellular polymeric substances (EPS) (Figure 1.4). Once the biofilm matures, it is metabolically unresponsive to antibiotics, which
limits the efficacy of antibacterial drugs for therapy, thereby requiring new high-price antibiotics discoveries.

Figure 1.4. Schematic formation of bacterial biofilm on the submerged medical device surface.\textsuperscript{16}

\section*{1.3. Antibiofouling strategies}

General biofouling on surfaces in marine and medical fields begins with conditioning layer formation to trigger early biofilm creation, which is a rapid and reversible process due to weak interactions between the films and the surfaces.\textsuperscript{6} Further fouling growth leads to irreversible settlement. To prohibit colonization, disruption of the initial state of fouling on surfaces is the critical strategy to prevent fouling. In the aquaculture industry, in the mid-1960s, self-polishing paint containing a biocide named tributyl tin (TBT) exhibited high efficiency in inhibiting the settlement of marine organisms on ship hulls. TBT was chemically bound with paint and then gradually released to be at the top of the coating surfaces to kill marine organisms. Unfortunately, the biocides also killed non-targeted species\textsuperscript{17,18} and were eventually banned from use in 2008.\textsuperscript{19} Later, copper-based paints and natural biocide-based coatings were developed, but they still had potentially adverse impacts on the marine environment. Paints containing natural biocides have been developed but required several toxicity studies before approval, which leads to higher
Currently, new strategies utilizing nontoxic, biocide-free coatings, which consist of intrinsic and unique compounds, have drawn attention to be studied for antifouling purposes. Polymer coatings have antifouling and antimicrobial properties from utilizing intrinsic functional groups that can resist protein adhesion and release the fouling organisms off the surfaces. Polymer coatings with low surface energy characteristics could release the fouling species off surfaces by water flow or mechanical cleaning. Moreover, high surface energy coatings provide unfavorable surfaces for biomacromolecule adhesion, preventing protein adhesion. For antimicrobial polymer coatings, cationic compound-based coatings have extensively been used as antibacterial agents to examine the efficacy of antimicrobial performance. They can kill bacteria in wide ranges of microorganisms such as Gram-positive bacteria, Gram-negative bacterial, or fungi. The positive charges of cationic compounds interact with negative charges on phosphate headgroups on the bacterial membrane through an electrostatic force. The hydrophobic segments of the cationic compounds destroy the cell walls by penetrating through the cell membrane, causing cytoplasm leakage and consequent death of bacterial cells. From the published articles, cationic polymers have exhibited superior antimicrobial activities to their small cationic molecules counterparts since they have relatively lower toxicity and have high density of charges in a polymer chain, promoting electrostatic interaction with bacterial membranes. Accordingly, polymer coatings incorporating functional groups with antifouling and antimicrobial properties have recently drawn attention to address these fouling issues.
CHAPTER 2

ANTIFOULING AND ANTIMICROBIAL POLYMER COATINGS

2. Introduction

2.1 Antifouling polymer coatings

As previously mentioned, some biocide-based paints were banned due to environmental hazards despite showing high antifouling performance. Alternative methods are needed. Both marine fouling and microbial settlements on surfaces start with the initial formation of a conditioning layer and further development of a biofilm as protein adsorb onto the surface. Such weak forces prefer to develop on a hydrophobic surface. Thus, hydrophilic coverages help inhibit adhesion, which is one of the concepts for the function of antifouling coatings. Currently, polymer coatings have been attractive since they can carry multiple functional groups, which can be hydrophobic, hydrophilic, or amphiphilic, in the same polymer chain, generating a variety of polymer coatings. The polymer coatings for antifouling application are either protein resistance or fouling release coatings. The former approach utilizes hydrophilic polymers, which have high surface energy, to disfavor protein adhesion, leading to the inhibition of settlement. Poly(ethylene glycol), PEG, is a well-known polymer that exhibits excellent resistance to protein and cell adhesion due to creating a hydration layer as a barrier in water, thereby preventing protein adsorption to the surface. On the other hand, low surface energy polymer coatings are where the attached species are easily removed from hydrodynamic shear flow before the strong attachment of biofilm develops. The common low surface energy polymers utilize silicone and fluorinated polymers since they have the lowest surface energy, favoring low adhesion strength between fouling organisms and the surface. However, both techniques do not allow the surfaces to impede accumulation permanently, some fouling colonies could still
penetrate the surfaces over time. An alternative method is to use an amphiphilic block copolymer coating on the bare surface to implement multiple mechanisms.

2.2 Amphiphilic block copolymer-based coatings

Amphiphilic block copolymers (BCP) consist of hydrophilic and hydrophobic components chemically bound in a single polymer chain. When amphiphilic block copolymers are cast on a surface, the immiscible segments segregate into discrete domains to minimize the interfacial surface energy. The chemical linkages prevent phase separation on the macroscale but instead form nanostructures that are the same size as biomacromolecules that adsorb. With the small self-segregated spaces and ambiguously heterogeneous domains on the surfaces, biomacromolecules or bacteria are challenged to adopt a suitable conformation to adsorb to the surface. Importantly, various polymer architectures, polymer compositions, and polymer functional groups generate a variety of surface phase separation patterns and domain sizes, consequently influencing antifouling properties (Figure 2.1). 30 Herein, the focus is on amphiphilic block copolymer-based surfaces as a promising coating for anti-fouling applications.
Figure 2.1. Schematic image of phase separation into nanostructure from amphiphilic copolymers with different architectures: a linear copolymer, a grafted copolymer, and a brush copolymer.\(^{30}\)

2.2.1 Structural reorganization of polymer coatings

The heterogeneous surfaces from nanostructured phase separation of amphiphilic block copolymers can prevent fouling organisms from adopting a suitable conformation to attach to the surfaces.\(^{30}\) To understand how phase segregation of BCPs on surfaces influence fouling resistance performance, the polymer films should generate self-assembled morphology and maintain their morphology despite being submerged under water, which often leads to rearranged morphology, to evaluate antibiofouling. Nevertheless, scientists have demonstrated that the polymer architectures and studied media (air/water) impact surface morphologies and domain sizes.\(^{31,37}\)

Martinelli et al. reported the rearrangement of polymer structures after sea water submersion of the comb-like block copolymer containing polystyrene (PS) as a hydrophobic domain and amphiphilic segment in the long grafted side chain containing ethoxylated fluoroalkyl surfactant Zonyl FSO-100 (SnSzm) (Figure 2.2A).\(^{31}\) Two-layer films were prepared on glycidyl-
functionalized glass substrate where the bottom layer was commercial poly(styrene-b-(ethylene-co-butylene)-b-polystyrene (SEBS) and the top was an amphiphilic copolymer blend with SEBS. The films were then treated by annealing to prevent delamination. Prior to water submersion, the morphologies of dry casted polymers were ordered and revealed spherical morphology for 56 wt% PS and parallel cylindrical morphology for 88 wt% PS. However, the ordered morphologies had significantly changed to be heterogeneous on the surface after submerged under water (Figure 2.2B). The morphology changes after submersion were ascribed to the exposure of the hydrophilic domains of polyethylene oxide to the water, while the hydrophobic domains of PS and fluoroalkyl component aggregated to avoid contacting the water interface (Figure 2.2A, schematic structural reorganization). The amphiphilic coatings were studied for their intrinsic resistance to the settlement of diatoms (Navicula). Generally, diatoms have strong adhesion strength to hydrophobic surfaces but weak interaction with hydrophilic surfaces. However, the antifouling assay demonstrated that diatoms adhered more strongly to the amphiphilic coatings that contained higher weight percentage of amphiphilic side chains. Such a result was attributed to the reconstruction of amphiphilic segments under water. Since well-ordered phase segregation was destroyed under water, using phase conformations to predict protein resistance performance was challenging.
Figure 2.2. Comb-like amphiphilic block copolymers containing PS as a hydrophobic domain and amphiphilic segment in the grafted chain (PS-b-PSz) blended with commercial SEBS and its phase separation behaviors. A) Schematic construction of amphiphilic block copolymer on the surface before and after water submersion. B) AFM phase images of PS-b-PSz with 56 wt% PS (top) in dry state (a) and wet state (b), and 88 wt% PS (bottom) of dry coatings (c) and after submersion (d).31

The reversible reorganizations of a linear amphiphilic block copolymer thin film containing poly(styrene-block-4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PS-b-PAEES) were studied in response to changing the environmental interface from air to water and vice-versa (Figure 2.3).32 The polymer rearrangement between hydrophobic (PS) and hydrophilic (PAEES) segments on a silicone surface were confirmed by near-edge X-ray absorption fine structure (NEXAFS) measurements. The PS-b-PAEES films were submerged under water at a temperature above the glass transition (T_g) of PAEES for 8 h and then cooled to room temperature prior to NEXAFS measurement. The films after water submersion were referred to as water-equilibrated films. The films were subsequently thermally annealed at 120 °C for 2 h before being analyzed by NEXAFS again and the films after this process were defined as a vacuum-equilibrated films (Figure 2.3B). NEXAFS spectra of a water-equilibrated film demonstrated PAEES enrichment on the outermost layer after water submersion and even after drying the film under vacuum at room temperature for 4 days (Figure 2.3C, step 1 and step 3). On the other hand, NEXAFS spectra of a vacuum-
equilibrated films exhibited PS enrichment on the surface after thermal treatment as evidenced by the significant PS peak (Figure 2.3C). This enrichment indicated polymer rearrangement from hydrophilic polymer exposure under water and then PS re-equilibration after thermal annealing. The reversible structural polymer rearrangements were also determined from water contact angle measurement of PS-b-PAEES thin films. Linear amphiphilic block copolymer coatings possessing flexible structures can rearrange in response to the external media, which is beneficial for stimuli-responsive polymer applications. However, the flexible architectures of the linear block copolymer coatings can lead to instability of the polymer morphology, consequently affecting antifouling performance of the material surfaces.

Figure 2.3. NEXAFS spectra of linear BCP of PS-b-PAEES demonstrating chemical composition on top the polymer surfaces after water submersion and thermal treatment. A) Linear BCP structure of PS-b-PAEES. B) Normalized Auger electron of NEXAFS spectra of BCP thin films after water submersion at 70 °C for 8 h, referred to as a water-equilibrated film, and subsequent thermal annealed films at 120 °C for 2 h, referred to as a vacuum-equilibrated film. C) NEXAFS spectra of BCP thin films after 2 cycles of water-equilibration and thermal-equilibration. The inserted NEXAFS spectra of BCP thin films analyzed right after water submersion for 8 h and then dried under vacuum at room temperature for 4 days.
2.3. Antifouling and antimicrobial polymer coatings containing quaternary ammonium polymers.

Quaternary ammonium polymers are contact-killing polymers for anti-microbial applications since the charges show high performance for killing bacteria, preventing successful biofilm formation and consequent fouling colonization. To prevent marine organism settlement on surfaces, Wen Jing et al. reported that cationic brush functionalized glass substrates exhibited effective prohibition of barnacle cyprid clusters, which are global macro-biofouling organisms, as evidenced by the bar chart, demonstrating 85% reduction of barnacle settlement compared to the uncoated glass substrates (Figure 2.4A). SEM images also supported the high resistance efficiency towards protein adsorption for the cationic brush coatings after submersion in flowing sea water for a week (Figure 2.4B). Denisa et al. demonstrated antifouling performance of nets coated with copolymers of poly(4-vinyl benzyl dimethylhexadecylammonium chloride), P(VBCHAM-co-AAx), cross-linked with poly(sodium 4-styrenesulfonate-co-glycidyl methacrylate), P(SSNa-co-GMAx), submerged in the sea during the summer when the environmental factors were suitable for fouling growth. The polymer-coated nets exhibited higher efficacy for fouling resistance than that of the uncoated nets after being submerged for 35 days (Figure 2.4C). Accordingly, cationic polymer coatings can inhibit the settlement of marine organisms, bacteria, and macro-scale species on the laboratory scale and natural fouling in the sea.
Figure 2.4. The investigation of anti-marine fouling activities of cationic polymer coatings. A) Bar chart demonstrated ratios of settled fractions of barnacle cyprids on quaternary ammonium functionalized glass substrate with a variety types of polymer coatings: GS-PHEMA was a nonionic hydrophilic coating, GS-PPFS was a nonionic hydrophobic coating, GS-PMETA was a cationic coating, GS-PNaSS was an anionic coating, and GS-PDMAPS was a zwitterionic coating. B) SEM images of the uncoated glass substrate (top) and cationic brush functionalized glass substrate (bottom) after submerged under the flowing sand-filtered seawater at the flow rate of 13.5 min\(^{-1}\) for a week.\(^{34}\) C) Photographs of uncoated and coated nets with copolymers of poly(4-vinylbenzyl chloride-co-acrylic acid), P(VBC-co-AAx), cross-linked with poly(sodium 4-styrenesulfonate-co-glycidyl methacrylate), P(SSNa-co-GMax) before and after submersion under sea water in the Saronic Bay of Greece in summer period for 35 days.\(^{35}\)

Interestingly, scientists have demonstrated that the alkyl chain lengths off the quaternary ammonium polymers impact the antibacterial efficacy due to the alkyl chain distribution and orientation on surfaces.\(^{36}\) He et al. reported that hierarchical architectures of brush block copolymers consisting of poly(sulfobetaine methacrylate) (PSBMA) as an antifouling polymer and
poly(quaternary ammonium salts) (PQAs) carrying different alkyl chain lengths as a contact-killing polymer influenced antifouling and antimicrobial performance on surfaces (Figure 2.5A).37 The PSBMA-b-PQAS coatings with a four carbon-alkyl chain demonstrated the best resistance to bacteria colonization and bacteria-killing efficiency (96.23%) (Figure 2.5B). However, the PSBMA-b-PQAS coatings with longer alkyl chains lengths reduced bactericidal performance due to accumulation of dead cells on the surfaces. On the other hand, PQAS-b-PSBMA coatings with the block order reversed and with an eight carbon-alkyl chain off PQAS revealed the best resistance to bacteria colonization and pathogen-killing performance. However, the coatings with PQAS bearing twelve-carbon alkyl chains exhibited inferior bactericidal performance to the coating counterparts with shorter alkyl chain lengths. This resulted from the rearrangement of the twelve-carbon alkyl chains to inside the polymer chains to avoid contacting water, consequently reducing the contact with bacteria on the surfaces.

Figure 2.5. A) Schematic brush block copolymer-functionalized silicon wafers containing PQAS-bottom layer and PSBMA-top layer, referred as to a PQAS-PSBMA coating (top) and PSBMA-bottom layer and PQAS-top layer, referred as to a PSBMA-b-PQAS coating (bottom) by having PQAS with different alkyl chain lengths: four-, eight- and twelve-carbon alkyl chains. B)
Fluorescence microscopy images of bacterial colonization of alive cell (green) and dead cell (red) on PQAS-PSBMA coatings and PSBMA-b-PQAS coatings with varied alkyl chain lengths of PQAS.\textsuperscript{37}

2.4. Antifouling and antimicrobial polymer coatings from bottlebrush architectures

Amphiphilic bottlebrush block copolymers (BBCPs) are composed of dense hydrophilic and hydrophobic polymer side chains grafted off a polymer backbone. The dense polymer arms intrinsically possess steric repulsion among the side chains, consequently stretching out the molecular backbone to adopt worm-like conformations. Thus, once robust architectures of BBCPs are cast onto material surfaces, they provide less flexible polymer surfaces with phase separated domains on the nanoscale. Xia et al. demonstrated creation of robust antifouling coatings consisting of zwitterionic polymer side chains of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC), cationic branches of quaternary poly(2-(dimethylaminoethyl) methacrylate) (PDMAEMA), and hydrophobic polymers of poly(methyl methacrylate) (PMMA) from three different architectures of the BBCPs: polymer B, polymer AB, and polymer ABA (Figure 2.6A).\textsuperscript{38} The polymer coatings prepared from drop casting of the BBCP solutions onto silica substrates exhibited strong adsorption through hydrogen bonding between the polymers and the substrates as demonstrated by the surface stability after being rinsed with 0.01 M HCl and 1 M NaCl solution, but lost mass after being rinsed with an alkaline solution (Figure 2.6B). For protein adhesion resistance performance, the BBCP-modified surfaces showed superior resistance to nonspecific protein adsorption of bovine serum albumin (BSA) as compared to unmodified surfaces and Pluronic F88-modified silica surfaces (linear triblock copolymer coatings) (Figure 2.6C). Additionally, the BBCP coatings with zwitterionic polymers of PMPC inhibited BSA adhesion (< 0.5 ng cm\textsuperscript{-2}) better than PMPC brush coatings (> 10 ng cm\textsuperscript{-2}). The higher antifouling performance of the BBCP coatings was attributed to forming a strong hydration barrier of PMPC side chains and
extended molecular BBCP structure due to steric repulsion between the polymer side chains. In addition to inhibiting protein adhesion, BBCPs-coated silica surfaces demonstrated prevention of bacterial settlement by reducing *E. coli* bacteria (*Escherichia coli*) settlement on the surfaces by more than 97% compared the bare silica surfaces (Figure 2.6D). From this literature, the extended polymer backbones of BBCPs increased the concentrations of polymer chain per area (chain nm²), thereby improving resistance to protein adsorption on the surfaces compared to brush polymer analog. Additionally, the suitable interaction between the polymer segments and the substrates is essential to consider for stable polymer coatings.

Figure 2.6. A) The structures of amphiphilic bottlebrush block copolymer carrying zwitterionic polymers of PMPC (blue highlight), and cationic polymers and hydrophobic polymer of PMMA (orange highlight) with three different architectures: polymer B, polymer AB, and polymer ABA. B) The mass loss of the BBCPs on silica surfaces representing stability of BBCP-modified surfaces
after being rinsed with NaOH, HCl, and NaCl. C) A comparison of antifouling coatings of ABA, AB, B-modified silica surfaces and unmodified surfaces against nonspecific protein adsorption of bovine serum (BSA), lysozyme, and β-Lactoglobulin (β-LG). D) Antibacterial performance of BBCPs coatings compared to the uncoated silica substrate against Escherichia coli monitored by fluorescence microscopy.\textsuperscript{38}

Recent literature reported bottlebrush-based antifouling coatings containing poly(L-lysine)−poly(N-(2-hydroxypropyl)-methacrylamide) (PLL-poly(HPMA)) using three different synthesis approaches, routes A, B, and C (Figure 2.7).\textsuperscript{39} All approaches generated similar BBCP coatings utilizing poly(HPMA) as antifouling polymers, while the charged polymers of PLL were an anchor layer interacting with the negative charges of silicon oxide surfaces. The BBCPs coatings synthesized from different methods contained a variety of polymer thickness, wettability of the coatings, and surface roughness, which depended on the methods used in sequential synthesis approaches. These three synthesis methods had advantages and disadvantages. The BBCP coating from route A had a thick and dense polymer coating which could be favorable for the stability of the coating, but it was hard to control the thickness and the length of the poly(HPMA) grafted from the surfaces. Likewise, the synthesis through route B provided the BBCP coatings with high thickness and density of the polymer layer but less stability due to fewer binding sites from the PLL layer to the surfaces. Well-defined BBCPs with controlled molecular weights (MW) were generated before grafting to the surfaces through route C. However, grafting a large polymer to the surface leads to significantly reduced coating thicknesses and reduced stability due to fewer binding sites to interact with the surface. Regardless of the characteristics of the resultant BBCP coatings, the coatings demonstrated high efficiency to inhibit BSA and lysosome protein adhesion onto the coatings as compared to the unmodified surfaces and PLL-coated coatings. Additionally, the PLL-coated coatings also showed superior resistance to protein adsorption as compared to the unmodified surfaces, suggesting that the positive charged layers in the BBCP coatings also reduced biomolecule adsorption. This publication suggested that the BBCPs coatings with cationic
polymer layers were successfully prepared by limiting the chain length of PLL (MW = 15000 – 30000 g mol\(^{-1}\)). The limited number of charges in the polymer-modified coatings may reduce the antifouling performance and the robustness of the coatings. However, the preparation of BBCP with a high density of positive charges is still challenging.

Figure 2.7. Synthesis schematic of polymer-modified silicon oxide substrates containing BBCPs of PLL-poly(HPMA) with different synthesis approaches: grafting from methods (route A), mixed approach (route B), and grafting-to (route C).\(^{39}\)

Quaternary ammonium polymers with different architectures have been produced by direct polymerization of cationic monomers via controlled radical polymerization in aqueous media\(^{40,41,42}\) or post-quaternization, which can be time-consuming and result in incomplete ammonium functionalization.\(^{43}\) Thus, current synthesis approaches can generate quaternary ammonium polymers or block copolymers with linear or brush-like architectures which possess flexible molecular chains. Creation of bottlebrush block copolymers carrying quaternary ammonium constituents have been reported in a few reports using a post-quaternization technique.\(^{38,44}\) Direct polymerization to generate dense quaternary ammonium bottle brush
homopolymers and block copolymers has not been reported yet due to solubility issues between
the charged polymers and organic solvent which are commonly used for polymerization, requiring
new techniques to synthesize these interesting materials.

2.5. Overview of Thesis Goals

Bottlebrush block copolymers are likely to generate robust and immobilized polymer
coatings due to the intrinsic steric repulsion among the polymer side chains extending the
molecular chain. Quaternary ammonium polymers demonstrate antifouling and antimicrobial
efficiency by being hydrophilic and bactericidal. Herein, we generated novel amphiphilic
bottlebrush block copolymers (BBCPs) with a high density of charged polymers. Then,
nanostructured morphologies from the self-assembly of BBCPs into thin films were explored to
understand how the symmetry of block compositions and the asymmetry of polymer side chains
influenced the resultant morphologies. Last, the stability of phase separated morphology was
studied after water submersion. The desired BBCPs are composed of quaternary ammonium
polymers as a hydrophilic segment chemically bound with polystyrene (PS), a hydrophobic
constituent. The quaternary ammonium functional groups serve as the antimicrobial agent and
PS is a lower surface energy polymer and is easy to be synthesized by numerous synthetic
methods.

Synthesis of polymers with a high density of charged polymers is challenging. They are
typically synthesized by a post-polymerization quaternization reaction which often leads to
incomplete quaternization and difficultly controlling the number of charges in a polymer chain.
Thus, the direct synthesis of dense cationic bottlebrush homopolymers and block copolymers has
not yet been reported prior to this work. We overcame the limitation by directly synthesizing
novel dense cationic bottlebrush homopolymers by ring opening metathesis polymerization
(ROMP) and investigating factors influencing the polymerization as provided in Chapter 3. After this success, a library of amphiphilic BBCPs were generated to further study the phase separated morphologies of thin films, which were analyzed by atomic force microscopy (AFM). The stability of the self-assembled morphology of the thin films was investigated before and after water submersion. Accordingly, the knowledge obtained from BBCP synthesis and its phase separation examination are reported in Chapter 4.
CHAPTER 3

CATIONIC BOTTLEBRUSH POLYMERS FROM QUATERNARY AMMONIUM MACROMONOMERS

BY GRAFTING-THROUGH RING-OPENING METATHESIS POLYMERIZATION

3.1. Introduction

3.1.1 Bottlebrush polymers

Bottlebrush polymers are macromolecules that consist of dense polymeric side chains grafted to a linear backbone. The inherent steric repulsion among the crowded neighboring side chains significantly influences how the polymer backbones’ behavior. The dense branches force the polymer backbone to stretch out, leading to a chain-extended conformation with worm-like behaviors (Figure 3.1).\textsuperscript{45,46,47,48,49} Unlike linear polymers, bottlebrush polymers have limited chain entanglement of the side chains, rendering rapid self-assembly and large domain sizes.\textsuperscript{50,51} This unique characteristic allows bottlebrush polymers and bottlebrush copolymers to be promising candidates in a variety of applications such as photonic crystals,\textsuperscript{52,53} nanocarriers of pharmaceutical agents,\textsuperscript{54,55} antifouling coatings,\textsuperscript{21,56,57} and stimuli responsive coatings.\textsuperscript{58,59,60,61}

Figure 3.1. Schematic of extended polymer backbone behaviors with a low density of grafted side chains (Left) to a high density of grafted side chains (Right) of bottlebrush polymers.
Four strategies exist to synthesize bottlebrush polymers, grafting-onto, grafting-from, transfer-to, and grafting through, each of which have advantages and shortcomings.\textsuperscript{62,63} The grafting-onto approach, which involves coupling separately pre-polymerized side chains and backbones, limits branch density.\textsuperscript{64,65,66} The grafting-from approach, which polymerizes side chains from a backbone initiator, can form bottlebrushes with long backbones, but can lead to side chain defects due to the increased likelihood of radical-radical coupling in some syntheses.\textsuperscript{67,68,69} The transfer-to technique is similar to the grafting-from approach except the chain transfer agent remains on the polymer backbone and active radicals exist on free polymer chains, which can eliminate side reactions present in the grafting-from method, however; termination defects still exist during polymerization.\textsuperscript{70,71} To prepare a completely dense bottlebrush polymer, the grafting-through method is commonly used by polymerizing macromonomers (MMs) with a reactive end group.\textsuperscript{61,72,73}

Grafting-through synthesis requires well-controlled polymerization techniques, which is particularly true for well-ordered architectures with high molecular weight (MW). Due to steric effects, initiation and propagation can be challenging with less reactive polymerizable end-groups such as methacrylates.\textsuperscript{74,75} As a result, ring-opening metathesis polymerization (ROMP) of high strained cyclic olefins is a powerful tool that has successfully produced well-defined bottlebrush polymers and copolymers with high molecular weights (MW), and a narrow molecular weight distribution (MWD) due to its wide functional group tolerance,\textsuperscript{76,77,78,79,80} fast polymerization rate, high MM conversion, typically by using the fast initiating third-generation Grubbs catalyst (G3).\textsuperscript{81}

3.1.2. Ring opening metathesis polymerization (ROMP)

ROMP is an olefin metathesis chain growth and is associated with metal-mediated carbon-carbon (C=C) double bond exchange. It is a powerful technique to create a vinylic polymer
backbone from ring strained cyclic monomers. The general driving force of ROMP is releasing the ring strain of cyclic monomers using a transition metal catalyst. With high enough ring strain (> 5 kcal mol\(^{-1}\)), the high strained cyclic olefins are readily polymerized to form polymers with a fast polymerization rate (Figure 3.2).\(^{119}\)

![Figure 3.2. ROMP reaction for converting cyclic monomers to an unsaturated polymer chain.\(^{119}\)](image)

The mechanism of ROMP occurs through a [2+2] cycloaddition reaction to form an intermediate called metallacyclobutane (Figure 3.3).\(^{119}\) For the initiation step, a transition metal alkylidene complex dissociates a ligand, providing an unstable complex with a vacant site. Subsequently, the active complex rapidly coordinates to an olefinic monomer to form the intermediate and rapidly transform to generate a monomer initiator containing a metal active center at the end. The propagation step involves the growing active polymer chains repeatedly in converting cyclic monomers into the polymer chains until all monomers are consumed, thereby achieving 100% monomer conversion. Last, the reaction is ceased to yield the metal-free polymers by adding the common terminating agent such as ethyl vinyl ether (EVE). Recently, ROMP has become a versatile tool to create the polymers with high molecular weights (MWs), diverse chain architectures and functional groups at high monomer conversion.
Without termination, ROMP is likely accompanied by undesirable reactions which are intermolecular and intramolecular chain transfer reactions, which increase the molecular weight dispersity (Figure 3.4). The former reaction shows that one active polymer chain end reacts with the unsaturated backbone of another polymer chain, yielding new polymers with different MWs and keeping the numbers of individual polymers in the system intact (Figure 3.4A). However, the latter, which is also called backbiting, provides reduced MWs of cyclic oligomers as a side product from the self-consumed active polymers with a metal alkylidene terminus (Figure 3.4B). Comprehensive understanding of the polymerization kinetics enables ROMP to overcome the drawbacks to generate desirable outcomes. Hence, considering characteristics of transition metal catalysts and strained cyclic monomers to achieve ROMP is needed.
Ruthenium alkylidene metathesis complexes are well known as the Grubbs catalyst family, which were developed by Grubbs and coworkers. They have low oxophilicity that renders stability toward moisture, air, and extensive functional groups, widening the diversity of possible polymers (Figure 3.5). The first common Grubbs catalyst is the 1st generation Grubbs catalyst (G1) which has relatively fast metathesis activity for small molecule and polymers production. However, the catalyst has the limitation of thermal degradation due to the phosphine ligands. Introducing a bulky and high electronic effect N-heterocyclic carbene (NHC) as a ligand to the ruthenium carbene complex, 2nd generation Grubbs catalyst (G2), improves the thermal tolerance and dissociation of trans PCy₃ ligand, thereby generating an excellent initiation rate, but moderate propagation rate. These properties lead to a polymerization that provides polymers with uncontrolled MW and high dispersity. Currently, polymer chemists have utilized a pyridine modified catalyst, 3rd generation Grubbs catalyst (G3), that has an excellent the initiation rate and the propagation rate, yielding the polymers with relative low dispersity (< 1.10). It expands the scope of polymerization to generate complex architectures of bottlebrush polymers and blocky
structures due to its living nature (no termination, fast metathesis reaction, and complete macromonomer conversion).

![Grubbs Catalyst Family](image)

**Figure 3.5.** The known Grubbs catalyst family used in ROMP.

Bicyclic olefins, norbornenes, are common monomers that have been used in ROMP since they have high ring strain energy (27.2 kcal mol$^{-1}$) from a double bond and a methylene bridge. Norbornene derivatives are readily polymerized under mild conditions to generate a variety of polymer architectures such as linear polymers, bottlebrush polymers, star polymers and block copolymers, depending on the types of norbornene monomers or norbornene macromonomers (MMs) used. For bottlebrush polymers derived from polymerizing MMs, different polymerizable terminal norbornenes or anchor groups of MMs influence the ROMP propagation rate due to steric and electronic effects (Figure 3.6).\textsuperscript{83,84,85} Additionally, heteroatoms of an (oxa)norbornene anchor group can partially interfere with the Grubbs catalyst to slow the ROMP propagation rate.\textsuperscript{86} Modification of the anchor group to an exo-norbornene structure can significantly increase the ROMP rate of MMs, yielding a narrow molecular weight distribution.\textsuperscript{84}
Figure 3.6. Kinetics study of ROMP of polystyrene macromonomers containing a variety of reactive norbornene end groups. A) The structures of different anchor groups reacting with G3, yielding bottlebrush polymer and their resting state influencing the rate of polymerization. B) Table summarized propagation rate constant of bottlebrush polystyrene polymerization from the PS MMs (MW of 3,000 g/mol) with different types of anchor groups and in varied medium solvent.

ROMP also has demonstrated a wide functional group tolerance to produce well-defined bottlebrush block copolymers with MMs carrying heteroatom functional groups through sequential ROMP. Well-controlled MMs are needed for well-defined bottlebrush polymers and they have been synthesized from a variety of techniques, which suppress side reactions of norbornene incorporation, such as reversible addition-fragmentation chain transfer (RAFT) polymerization, atom transfer radical polymerization (ATRP), living anionic polymerization (LAP), ring-opening polymerization (ROP), and other types of polymerizations. Thus, a wide library of potential MMs exists to create new bottlebrush polymers and copolymers.

One class of macromonomers that has been difficult to directly polymerize by grafting-through ROMP are those that contain dense quaternary ammonium groups. Such polymerizations have not been reported in open literature to the authors’ knowledge. The synthesis of cationic bottlebrush polymers by a grafting-onto approach through a combination of ROMP and click chemistry has only grafted a limited number of quaternary ammonium polymer branches to the backbone. New methods are still needed to synthesize densely grafted cationic bottlebrush
polymers. Due to the high reactivity of ROMP, it should be possible to overcome the limitations of these techniques to produce well-defined quaternary ammonium bottlebrush polymers. However, for a well-controlled ROMP, the quaternary ammonium macromonomers and resulting polymers should be homogeneous during the polymerization, which can be challenging as organic solvents such as dichloromethane (DCM) or tetrahydrofuran are typically needed when using the G3 catalyst. As a result, only linear polymers containing cationic functional groups have been prepared via ROMP by directly polymerizing norbornene derivatives containing quaternary ammonium groups. The ROMP of quaternary ammonium macromonomers through a grafting-through approach, yielding bottlebrush structures, has not yet been reported.

Ligand environments around the ruthenium metal center impact the metathesis activity of the catalyst. Halide ligand types can improve the initiation rate constant ($k_i$) by exchanging chloride ligands for bromide or iodide ligands; however, this exchange decreases the propagation rate constant ($k_p$) of the given catalyst initiator. Halide ligand exchange has been observed during synthesis of cationic polymers from cationic exo-7-norbornene derivatives using the first-generation Grubbs catalyst for ROMP. Cationic monomers with bromide counter-ions polymerized slower than their chloride counterparts but had a narrower MWD and still followed first-order kinetics in monomer. Since halide counter-ion concentration due to monomer can significantly affect polymerization, even higher halide concentrations from macromonomers are expected to change polymerization kinetics and behavior. Hence, studies are needed to understand the effect of halide counter ions on ROMP of cationic macromonomers.

To expand the available bottlebrush polymer structures, herein our group reports a technique to synthesize cationic bottlebrush polymers and block copolymers with a full density of quaternary ammonium side chains through a grafting-through approach. Quaternary ammonium macromonomers were prepared through reversible addition-fragmentation chain transfer (RAFT)
polymerization of tertiary amine monomers, resulting in polymerizable norbornene-capped macromonomers (Scheme 3.1). These macromonomers were then further modified with an alkyl halide to produce quaternary ammonium macromonomers. We hypothesized and demonstrated that bottlebrush polymers could be prepared by ROMP utilizing the G3 catalyst in DCM. Halide counter ions associated with the quaternary ammonium moiety affected the rate of ROMP. Moreover, various MWs of MMs and alkyl group chain lengths off the ammonium were investigated for their effects on ROMP. These kinetic studies of the ROMP of quaternary ammonium MMs demonstrated controlled polymerization so that amphiphilic bottlebrush polymers could be generated by sequential macromonomer addition during ROMP.

3.2. Experimental details

3.2.1 Materials

All chemicals and solvents were obtained from commercial sources and used as received unless otherwise stated. Inhibitors were removed from monomers immediately prior to use where styrene monomer (St) was purified by passing through a basic alumina column and 2-(dimethylamino)ethyl acrylate (DMAEA) was purified by vacuum distillation. 2,2′-Azobis(2-methylproponitrile) (AIBN) was recrystallized in methanol before use. N,N′-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), lithium aluminium hydride (LiAlH₄), inhibitor free anhydrous tetrahydrofuran (THF), and ACS grade dichloromethane (DCM), were used as received. The third generation Grubbs catalyst, (H₂IMes)-(pyr)₂(Cl)₂RuCHPh (G₃), and 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT CTA) were prepared following literature procedures.

3.2.2. Characterization

3.2.2.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H-NMR spectra were obtained either using a Varian Inova 400 MHz NMR spectrometer or a Bruker Avance NEO 500 MHz NMR spectrometer in deuterated chloroform (CDCl₃) solvent. The analysis condition undertaken at 25 °C with 5 s and delay time 128 for Varian Inova 400 MHz NMR spectrometer, and delay time 64 for Bruker Avance NEO 500 MHz NMR spectrometer. The sample solution preparation was dissolving the sample (5-9 mg) in 0.6 mL deuterated chloroform.

3.2.2.2. Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was conducted in dimethylformamide (DMF) containing 0.5 wt% LiBr as the mobile phase with flow rate 1.0 mL/min at 70 °C. The mobile phase...
was filtered through 0.45 μm polypropylene (PP) membrane prior use. SEC analysis was performed by three Phenogel columns in series with different pore sizes (Phenomenex columns, 50Å, 10^3Å, and 10^6Å), using a refractive index detector and calibration curves from linear polystyrene standards. The average number molecular weight (Mₙ) obtained from SEC was determined using the hydrodynamic volume of the synthesized polymers relative to that of linear polystyrene and was not expected to give the exact molecular weight of the bottlebrush polymers due to this assumption. Prior SEC analysis, SEC samples were prepared at approximately 3.0 mg/mL in DMF with 0.5 wt% LiBr salt. The homogeneous solution was filtered through a 0.2 μm filter to confirm particle contamination.

3.2.3. Synthetic methods

3.2.3.1. Synthesis of exo-5-norbornene-2-methanol

![Synthesis of exo-5-norbornene-2-methanol](image)

Synthesis of exo-5-norbornene-2-methanol was adapted from a literature method.¹⁰⁷ Endo/exo norbornene-5-carboxylic acid (9.667 g, 69.99 mmol) was dissolved in a solution of NaHCO₃ (6.714 g, 79.92 mmol) and 100 mL reverse osmosis (RO) water in a 500 mL round bottom flask equipped with a stir bar. A solution of I₂ (15.998 g, 63.03 mmol) and KI (17.530 g, 105.60 mmol) in 200 ml RO water was stirred overnight to dissolve the iodine. The I₂/KI solution was added dropwise to the endo/exo norbornene acid by addition funnel until the solution retained a dark brown color. The dark brown mixture was vacuum filtered, and the filtrate was extracted with diethyl ether until the aqueous layer remained a light-yellow color. The aqueous layer was decolorized using 10% Na₂S₂O₃ solution in RO water and acidified to pH of 2 with 1N H₂SO₄. The exo-product was extracted with diethyl ether (6 x 200 mL), the collected organic layer was dried.
with anhydrous Na$_2$SO$_4$, and concentrated with vacuum evaporation to generate an off-white solid. The solid was further purified by column chromatography in 30:70 mixture of solvent of ethyl acetate to hexane. Next, the reduction reaction of obtained exo-5-norbornene-2-carboxylic acid with LiAlH$_4$ in dry THF was performed following the literature procedure to obtain the pure exo-5-norbornene-2 methanol (61% yield).

$^1$H-NMR (CDCl$_3$, 400 MHz) of exo norbornene-5-carboxylic acid: δ 6.13 (m, vinylic protons, 2H), 3.12 (s, 1H), 2.95 (s, 1H), 2.28 (m, 1H), 1.94 (m, 1H), 1.54 (d, 1H), 1.32-1.48 (m, 2H).

$^1$H-NMR (CDCl$_3$, 500 MHz) of exo-5-norbornene-2 methanol: δ 6.08 (m, vinylic protons, 2H), 3.70 (m, 1H), 3.54 (m, 1H), 2.82 (s, 1H), 2.75 (s, 1H), 1.69 (m, 1H), 1.62 (s, -OH, 1H), 1.18-1.38 (m, 3H), 1.13 (m, 1H).

3.2.3.2. Synthesis of NB-RAFT CTA

NB-RAFT CTA synthesis followed an adapted literature procedure for a coupling reaction between exo-5-norbornene-2-methanol and DDMAT CTA using DCC and DMAP in DCM. In a 100 mL round bottom flask, exo-5-norbornene-2-methanol (0.796 g, 6.4 mmol), DDMAT CTA (2.921 g, 8.1 mmol), DMAP (0.079 g, 0.65 mmol) were dissolved in 40 mL anhydrous DCM. DCC (1.785 g, 8.7 mmol) was added to the solution to yield a cloudy mixture, which was stirred for 15 hours. The solid was vacuum filtered off, the yellow liquid filtrate was concentrated by rotary evaporation, and purified using column chromatography with 75:25 mixture of DCM:hexane to obtain the NB-RAFT CTA as a yellow liquid (79% yield). The synthesized NB-RAFT CTA was analyzed by $^1$H-NMR spectroscopy in CDCl$_3$ to confirm its structure (Figure A.1).
3H-NMR (CDCl₃, 400 MHz) of NB-RAFT CTA: δ 6.07 (m, vinylic protons, 2H), 4.20 (dd, 1H), 3.95 (t, 1H), 3.28 (t, 2H), 2.82 (s, 1H), 2.67 (s, 1H), 1.71 (s, 6H), 1.60 (m, 2H), 1.25 (m, 20 H), 0.88 (t, 3H).

3.2.3.3 Synthesis of poly(dimethylamino ethyl acrylate) macromonomer via RAFT polymerization (NB-PDMAE)

RAFT polymerization was performed with a 40:1:0.05 molar ratio of monomer:NB-RAFT CTA:AIBN in anhydrous THF. DMAEA monomer (38.8 g, 271.0 mmol), NB-RAFT CTA (3.184 g, 6.77 mmol), AIBN (0.056 g, 0.34 mmol), and anhydrous THF (20.6 mL) were mixed in a 250 mL Schlenk round bottom flask equipped with a magnetic stir bar. The yellow mixture was degassed by three freeze-pump-thaw cycles and then submerged in preheated oil bath at 52 °C for 10 hours to reach 35% DMAEA conversion. The solution was quenched by immersing the flask in an ice bath for 30 minutes. Most of the unreacted DMAEA monomer was removed by vacuum distillation at 65 °C. Prior to vacuum distillation, BHT (0.75 g, 3.40 mmol) was added to the solution to suppress further polymerization during heating. This concentrated crude NB-PDMAEA polymer solution was further purified by precipitation from THF into dry ice chilled hexanes 6 times and the collected polymer was dried under vacuum without heating to yield NB-PDMAEA with some BHT contaminant that was carried over to the next step. The crude polymer was analyzed by 3H NMR spectroscopy in CDCl₃ (Figure 3.7). The number of repeat units per chain was calculated by end group analysis, using the relative integration of the repeat unit methylene protons (4.15 ppm) and norbornenyl alkene protons (6.09 ppm) to obtain 14 DP at 35% conversion. The yellow liquid macromonomer with 14 DP was defined as NB-PDMAEA₁₄. A higher molecular weight NB-
PDMAEA MM was synthesized following the procedure above, except the polymerization was run for 16.5 hours to reach 45% DMAEA conversion and yielded a 19 DP polymer defined as NB-PDMAEA\textsubscript{19}.

3.2.3.4. Synthesis of poly(dimethylamino ethyl acrylate) polymer without norbornene end groups via RAFT polymerization (PDMAEA)

\[
\begin{array}{c}
\text{HO} \\
\text{S} \\
\text{S} \\
\text{10} \\
\text{N}
\end{array}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
+ \begin{array}{c}
\text{CH}_{2}=\text{CH}-\text{CO}-
\end{array}
\xrightarrow{\text{AIBN}}
\begin{array}{c}
\text{HO} \\
\text{S} \\
\text{S} \\
\text{10} \\
\text{N}
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\text{O} \\
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\end{array}
\]

DMAEA monomer (5.846 g, 40.8 mmol), DDMAT CTA (0.372 g, 1.02 mmol), AIBN (0.008 g, 0.05 mmol), and anhydrous THF (3.1 mL) were mixed in a 20 mL ampule equipped with a magnetic stir bar. The yellow mixture was degassed by three freeze-pump-thaw cycles and then submerged in preheated oil bath at 72 °C for 1.75 hours. After quenching in an ice bath, the crude PDMAEA polymer solution was purified by precipitation from THF into dry ice chilled hexane 6 times and the collected polymer was dried under vacuum without heating. The polymer crude was analyzed by \textsuperscript{1}H NMR spectroscopy in CDCl\textsubscript{3} (Figure S4). The number of repeat units per chain was calculated by end group analysis, using the relative integration of the repeat unit methylene protons (4.15 ppm) and methylene protons of the DDMAT CTA chain end (3.34 ppm) to obtain 24 DP at 60% conversion. The yellow liquid macromonomer was defined as PDMAEA\textsubscript{24}.

3.2.3.5. Synthesis of polystyrene macromonomer via RAFT polymerization (NB-PS)

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{S} \\
\text{10}
\end{array}
\begin{array}{c}
\text{CH}_{2}=\text{CH}-
\end{array}
\xrightarrow{\text{AIBN}}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{S} \\
\text{10}
\end{array}
\begin{array}{c}
\text{CH}_{2}=\text{CH}-
\end{array}
\]
RAFT polymerization was performed with a 400:1:0.05 molar ratio of monomer:NB-RAFT CTA:AIBN in anhydrous THF. St monomer (90.51 g, 869.0 mmol), NB-RAFT CTA (1.021 g, 2.17 mmol), AIBN (0.018 g, 0.11 mmol), and anhydrous THF (50.0 mL) were mixed in a 250 mL Schlenk round bottom flask equipped with a magnetic stir bar. The yellow mixture was degassed by three freeze-pump-thaw cycles and then submerged in a preheated oil bath at 52 °C for 40 minutes to reach 4.5% St conversion. The solution was quenched by immersing the flask in an ice bath for 30 minutes. The unreacted St monomer was removed by multiple precipitations from THF into dry-ice chilled methanol and dried under vacuum at room temperature until no St monomer was detected by ¹H NMR spectroscopy. The yellow solid NB-PS MM was analyzed by ¹H-NMR spectroscopy in CDCl₃ (Figure S5) and SEC. The degree of polymerization was calculated to be 17 DP by end group analysis, using the relative integration of styrene repeat unit protons at 6.20-7.20 ppm and norbornenyl alkene protons at 6.07 ppm. The resultant polymer was defined as NB-PS₁₇.

3.2.3.6. General procedure for quaternization reaction to synthesize quaternary ammonium macromonomers (NB-PDMAEA-C#·X)

All quaternary ammonium macromonomers were synthesized by reacting NB-PDMAEA MMs with either 1-bromohexane, 1-iodohexane, or 1-bromododecane in ethanol at 52 °C to achieve NB-PDMAEA-C6·Br, NB-PDMAEA-C6·I, and NB-PDMAEA-C12·Br, respectively. Both NB-PDMAEA₁₄ and NB-PDMAEA₁₉ were used to synthesize these various quaternary ammonium...
macromonomers using the typical procedure below. The same procedure was used to synthesize PDMAEA-C6-Br24 and PDMAEA-C6-I24 from PDMAEA24 as well.

In a typical reaction, the NB-PDMAEA was reacted with a 21 molar excess of alkyl-halide in relation to moles of the macromonomer at a 0.3 M macromonomer concentration in absolute ethanol at 52 °C until complete conversion of amines was confirmed by 1H NMR spectroscopy, which typically required reaction periods greater than 44 h. All samples were purified by precipitating from ethanol into dry-ice chilled ethyl acetate at least 3 times and followed by precipitation from DCM into dry-ice chilled hexanes at least once. The purified MMs were analyzed by 1H-NMR spectroscopy in CDCl3 to confirm removal of the excess alkyl-halide. The yellow solid quaternary ammonium MMs were dried under vacuum at room temperature. The resultant MMs were defined as NB-PDMAEA-C#-Xp where # is the number of carbons in the added alkyl chain, X is halide counter ions, and ‘p’ is the DP of the quaternary ammonium macromonomers.

As an example detailed reaction, NB-PDMAEA-C6-Br14 was prepared by mixing NB-PDMAEA14 (1.13 g, 0.46 mmol), 1-bromohexane (1.35 mL, 9.59 mmol), and absolute ethanol (1.5 mL) in 20 mL scintillation vial equipped with a magnetic stir bar. The yellow solution was heated at 52 °C for 44 hours. The resultant NB-PDMAEA-C6-Br14 was purified by precipitation from ethanol into dry-ice chilled ethyl acetate 3 times and then precipitation from DCM to dry-ice chilled hexanes once. The yellow solid quaternary ammonium macromonomer was dried in vacuum at room temperature. 1H-NMR analysis (400 MHz, CDCl3): 6.09 ppm (2 H, norbornenyl alkene), 4.74 ppm (-COO-CH2-, 30.34 H, methylene group in repeat unit), 4.15 ppm (-CH2-CH2-N(C6H13)(CH3)2, 35.08 H, methylene group in repeat unit), 3.73 ppm (-CH2-CH2-N(CH2-C6H11)(CH3)2, 34.10 H, methylene group in repeat unit), 3.47 ppm (-CH2-CH2-N(C6H13)(CH3)2, 123.87 H, methyl group in repeat unit), 1.25 ppm (18 H, -(CH2)9-CH3, methylene groups of a CTA chain end), 0.88
ppm (-CH$_2$-N(CH$_3$)$_2$(C$_5$H$_{10}$-CH$_3$), and -(CH$_2$)$_9$-CH$_3$), methyl groups associated with the added alkyl halide agents in repeat units and a CTA chain end, respectively) (Figure S6). $^1$H NMR spectra of the other quaternary ammonium macromonomers and polymers are shown in Figures A.2 – S.9.

3.2.3.7. Synthesis of cationic bottlebrush homopolymers from quaternary ammonium macromonomers via ROMP

In a typical ROMP experiment, which was undertaken in a glove bag under N$_2$ atmosphere, the following materials were prepared before transferring to the glove bag. A dry 4 ml vial with a rubber septum cap containing MM (for example, 50 equivalents, 0.0658 g, 0.0137 mmol of NB-PDMAEA-C6-Br$_{14}$) and a small stir bar that was purged with N$_2$ gas for 30 minutes. A 20 mL ampule with 10 mL DCM that was degassed by three freeze-pump-thaw cycles. All materials were then transferred to the glove bag under N$_2$ gas. The desired amount of degassed DCM (280 µL DCM) to reach a specific initial MM concentration ([MM]$_0$ = 0.03 M) was added to the vial by a N$_2$-purged syringe to dissolve the quaternary ammonium macromonomers. A stock solution of G3 (1 mg/mL) was freshly prepared in the glove bag in degassed DCM. Next, 200 µL of this G3 solution (1 equivalent, 0.0002 g, 2.75 x 10^{-4} mmol) was immediately injected into the macromonomer solution to start ROMP and to give an initial G3 concentration ([G3]$_0$) of 5.73 x 10^{-4} M in a fixed total DCM volume of 480 µL. For kinetic studies, 50 µL aliquots at different reaction times were taken out and quenched by adding them to a 0.3 mL ethyl vinyl ether solution in 0.6 mL DCM in
the glove bag. Each aliquot was purged N\textsubscript{2} to eliminate the excess ethyl vinyl ether and DCM and then dried under vacuum overnight. Bottlebrush polymerization was analyzed via \textsuperscript{1}H-NMR spectroscopy in CDCl\textsubscript{3} and SEC in DMF with 0.5 wt\% LiBr as the mobile phase. MM conversion was calculated from the relative integration of norbornene olefin peak (6.09 ppm) to methylene protons in the repeat units (4.76 ppm) that were assumed to not shift significantly during polymerization. The unreacted MMs were eliminated by precipitation from DMF into dry-ice chilled diethyl ether until no trace of unreacted norbornene was present as indicated by a peak at 6.09 ppm in the \textsuperscript{1}H NMR spectra.

The other MM ROMPs were conducted using the same procedure above by preparing MM:G3 molar ratios of 50:1 with [MM]\textsubscript{0} = 0.03 M and [G3]\textsubscript{0} = 5.73 x 10\textsuperscript{-4} M. Homopolymerization of NB-PDMAEA-C6-Br\textsubscript{14} with varied MM:G3 values of 25:1, 74:1, 100:1 and 200:1 followed the general ROMP procedures above by changing the mass of quaternary ammonium MMs in a fixed 480 \textmu L of DCM and constant [G3]\textsubscript{0} of 5.73 x 10\textsuperscript{-4} M. The ROMP of NB-PDMAEA-C6-Br\textsubscript{14} with the presence of non-norbornene terminated homopolymers PDMAEA-C6-Br\textsubscript{24} and PDMAEA-C6-I\textsubscript{24} was conducted as above aside for the following changes. The PDMAEA homopolymers (0.004 mmol, 0.008 M of the polymer) were mixed with G3 (2.75 x 10\textsuperscript{-4} mmol G3) in DCM for two minutes prior to addition to the NB-PDMAEA-C6-Br\textsubscript{14} macromonomer in solution (0.007 mmol, 0.015 M of [MM]\textsubscript{0}) to give [G3]\textsubscript{0} equal to 5.73 x 10\textsuperscript{-4} M. Aliquots were taken and quenched as described above.

3.2.3.8. Halide ligand exchange of G3 with quaternary ammonium polymers without norbornene end groups
The polymer solution was prepared under nitrogen atmosphere by dissolving PDMAEA-C6-Br24 (0.0288 g, 0.0037 mmol) in 0.15 mL degassed DCM. The G3 catalyst solution was prepared by dissolving G3 (0.0054 g, 0.0074 mmol) in 0.1 mL degassed DCM. The G3 solution was added to the polymer solution by a syringe to start the halide ligand exchange. Crude reaction solution (0.13 mL) was removed after 2 minutes and the rest of the mixture was stirred for 2 h. Both crude samples were concentrated by purging N2, dried under vacuum for 30 minutes, and then were analyzed by 1H-NMR spectroscopy in CDCl3. The halide ligand exchange of G3 with PDMAEA-C6-I24 was performed using the same procedure as above using PDMAEA-C6-I24 (0.0330 g, 0.0037 mmol) and G3 (0.0054 g, 0.0074 mmol).

3.2.3.9. General procedure for amphiphilic bottlebrush block copolymer synthesis via ROMP

For these syntheses, the glove bag techniques described above were used to prepare the reagents and perform the reactions. To synthesize bottlebrush block copolymers with MM1:MM2:G3 molar ratios of 25:25:1, the first MM solution was prepared at [MM]₀ = 0.015 M (480 µL DCM in reaction mixture) and then, G3 solution was added to give [G3]₀ of 5.73 x 10⁻⁴ M. Before adding the second MM, a 50 µL crude sample of the first block was taken and quenched with ethyl vinyl ether solution (0.3 mL ethyl vinyl ether in 0.6 mL DCM). The second solution of MM with [MM]₀ = 0.011 M to give a MM:G3 of 25:1 was added to the first polymer solution and polymerized to yield bottlebrush block copolymers. The crude samples of each block were
extracted and quenched in ethyl vinyl solution and analyzed by ¹H-NMR spectroscopy to find % MM conversion and SEC to find $M_n$ and dispersity.

Specifically, to synthesize PDMAEA-C6-Br$_{14}$-b-PS$_{17}$, 0.0329 g (0.007 mmol) of NB-PDMAEA-C6-Br$_{14}$ MM was added to a 4 mL vial with a septa cap, purged with $N_2$ for 30 minutes, and dissolved in 280 µL of degassed DCM. The PS MM stock solution was created by dissolving 0.0154 g (0.007 mmol) of NB-PS$_{17}$ in 170 µL degassed DCM. A fresh stock solution of 1 mg/ml G3 in DCM was prepared and 200 µL of the G3 stock solution (1 equivalent, 0.0002 g, $2.75 \times 10^{-4}$ mmol) was immediately added to quaternary ammonium MM solution to start the first block polymerization which ran for 60 minutes. Then, the PS MM solution was added to the reaction mixture by a $N_2$ purged syringe to polymerize the second block. The reaction was run for 30 minutes and quenched by adding ethyl vinyl ether solution to the vial by a syringe. The crude samples were purged $N_2$ to eliminate excess ethyl vinyl ether and then dried in vacuum at room temperature overnight before analysis. The $M_n$ of PDMAEA-C6-Br$_{14}$-b-PS$_{17}$ was determined by SEC to be 60,000 g/mol with a $Đ$ of 1.40. For bottlebrush block copolymerization of PS$_{17}$-b-PDMAEA-C6-Br$_{14}$, where PS MMs were used for the first block, the procedure followed the above method except the PS MM polymerization was run for 3 minutes before adding the quaternary ammonium MM which was run for 60 minutes before quenching. The $M_n$ of PS$_{17}$-b-PDMAEA-C6-Br$_{14}$ was determined by SEC to 70,000 g/mol with a $Đ$ of 1.26.

3.3. Results and Discussion

3.3.1. Synthesis of NB-PDMAEA and NB-PS macromonomers via RAFT polymerization

Tertiary amine MMs were synthesized by RAFT polymerization using a norbornene functionalized chain transfer agent (NB-RAFT CTA) (Scheme 3.1A). A low loading of AIBN at 52 °C was used to avoid generating a high number of active radical chains, which subsequently
suppressed chain end coupling or termination side reactions to generate MMs with one norbornene group (NB) per chain. Also, low % conversions (35 – 45%) were targeted to avoid the polymerization of the norbornene groups.\textsuperscript{108,109,110} The polymerization characteristic and resulting polymers were analyzed by size exclusion chromatography (SEC) and \textsuperscript{1}H-NMR spectroscopy. \textsuperscript{1}H-NMR spectra confirmed that no undesired reactions took place during RAFT polymerization as indicated by good agreement of relative integration ratios of the norbornene olefin peaks at 6.08 ppm and the peaks at 3.33 and 0.88 ppm associated with the RAFT chain transfer agent at the other end of the chain (Figures 3.7). SEC analysis showed a symmetric unimodal peak with a $D$ of 1.36 without shoulders at higher molecular weight that would indicate chain end coupling. With the low monomer conversion, a significant amount of unreacted DMAEA monomers remained, which made purification by precipitation challenging and resulted in low polymer yields. To address this, vacuum distillation was employed to reduce the excess monomers prior to precipitation. Before distillation, BHT, which is a well-known radical scavenger, was added to suppress further radical polymerization while heating at 65 °C during vacuum distillation. After distillation, the monomer concentration was significantly reduced so that precipitation could be used to remove the remaining monomer. \textsuperscript{1}H-NMR spectra and SEC chromatograms were consistent before and after distillation (Figure 3.8), demonstrating that this purification did not alter the polymers. After precipitation, BHT still remained in the NB-PDMAEA, but it could be eliminated during the subsequent purification of quaternary ammonium MMs. The larger PDMAEA macromonomers were prepared with the same procedure and ran at the longer reaction time to yield the polymer with degree polymerization (DP) of 19 referred to as NB-PDMAEA\textsubscript{19} (Figure 3.7). The DP of macromonomers were determined from \textsuperscript{1}H-NMR spectrum by end group analysis, utilizing the relative integration ratios of the peak corresponding to the repeat units to the proton peak of the chain end. For example, using integration of methylene protons adjacent
to the RU ester functional group in at 4.15 ppm and norbornene olefin protons of the chain end at 6.08 ppm provided MMs with DPs of 14 and 19 as seen in Figure 3.7, respectively.

Figure 3.7. $^1$H-NMR spectra of the precipitated norbornene-functionalized PDMAEA MMs with BHT contamination with different MWs. A) $^1$H-NMR spectrum of NB-PDMAEA with DPs of 19 and B) $^1$H-NMR spectrum of NB-PDMAEA with DPs of 14 synthesized by RAFT polymerization.
Figure 3.8. SEC chromatogram of tertiary amine MMs of NB-PDMAEA₁₄ synthesized via RAFT polymerization before vacuum distillation (black line, $M_n$ obtained from SEC = 1,200 g/mol and a $Đ = 1.36$) and after vacuum distillation (red dash line, $M_n$ = 1,200 g/mol and a $Đ = 1.42$) at 65 °C.

Polystyrene macromonomer (NB-PS) was also prepared by RAFT polymerization with low loading AIBN content at 52 °C to afford well-defined structures of NB-PS MM. The DP was calculated from end group analysis by employing proton resonance of PS in the repeat units at 6.25-7.30 ppm and norbornene olefin protons of the end group at 6.07 ppm, providing the MMs with DP of 17 (Figure 3.9).

Figure 3.9. $^{1}H$-NMR spectrum of purified NB-PS macromonomer with 17 DP (NB-PS₁₇)
3.3.2. Synthesis of quaternary ammonium macromonomers

The modification from tertiary amine MMs to quaternary ammonium MMs was carried out with alkyl halide agents through a straightforward quaternization reaction (Scheme 3.1B). The completion of functionalization was monitored by $^1$H-NMR spectroscopy. As a result, $^1$H-NMR spectra confirmed quaternary ammonium group formation as the methylene protons adjacent to the RU ester functional group (-COO-CH$_2$-, 4.76 ppm), methylene protons adjacent to the amine (-CH$_2$-CH$_2$-N-(CH$_3$)$_2$, 4.15 ppm), and ammonium methyl groups (-CH$_2$-CH$_2$-N-(CH$_3$)$_2$, 3.40 ppm) shifted downfield due to the electron deficient quaternary ammonium group in addition to the appearance of new peaks due to the added alkyl chain (Figure 3.10). The relative integrations of protons between the end groups and backbone confirmed complete conversion to quaternary ammonium groups. SEC analysis of quaternary ammonium MMs in DMF alone was not successful due to physical interactions between the polymers and SEC analytical columns so 0.5 wt% LiBr was added to the mobile phase to improve separation by SEC. The SEC chromatograms demonstrated unimodal curves for quaternary ammonium macromonomers at shorter elution times compared to the curves of tertiary amine MMs, indicating that quaternization changed the hydrodynamic radius of the resultant MMs and did not alter the distribution shape of charge-free MMs. Additionally, SEC provided M$_n$ values that corresponded to larger sizes of quaternary ammonium MMs compared to that of precursor of tertiary amine MMs (Figure 3.11). Likewise, M$_n$ results of the MMs with twelve pendent groups were also higher than that with six carbon counterparts. All quaternary ammonium MMs were soluble in DCM, but insoluble in THF, which are the common solvents used for ROMP. Through this synthesis methodology, a library of MMs (summarized in Table 3.1) was created to study their ROMP.
Figure 3.10. $^1$H-NMR spectra of purified macromonomers. A) quaternary ammonium MM with six carbon alkyl pendant group and bromide counter ions (NB-PDMAEA-C6-Br$_{14}$) and B) tertiary amine MM with DP of 14 (NB-PDMAEA$_{14}$) with BHT contamination.
Table 3.1. Characteristics of macromonomers (MMs) synthesized by sequential RAFT polymerization and amine quaternization with alkyl halide agents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macromonomer</th>
<th>$M_n(SEC)$ $[^a]$ [g mol$^{-1}$]</th>
<th>$M_n(NMR)$ $[^c]$ [g mol$^{-1}$]</th>
<th>DP$[^d]$</th>
<th>$D$ $[^e]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM-1</td>
<td>NB-PDMAEA$_{14}$</td>
<td>1200</td>
<td>2500</td>
<td>14</td>
<td>1.36</td>
</tr>
<tr>
<td>MM-2</td>
<td>NB-PDMAEA$_{12}$</td>
<td>1900</td>
<td>3200</td>
<td>19</td>
<td>1.41</td>
</tr>
<tr>
<td>MM-3</td>
<td>NB-PDMAEA-C6-Br$_{16}$</td>
<td>2600</td>
<td>4500</td>
<td>14</td>
<td>1.36</td>
</tr>
<tr>
<td>MM-4</td>
<td>NB-PDMAEA-C6-I$_{14}$</td>
<td>2200</td>
<td>5400</td>
<td>14</td>
<td>1.36</td>
</tr>
<tr>
<td>MM-5</td>
<td>NB-PDMAEA-C12-Br$_{14}$</td>
<td>3600</td>
<td>6000</td>
<td>14</td>
<td>1.38</td>
</tr>
<tr>
<td>MM-6</td>
<td>NB-PDMAEA-C6-Br$_{19}$</td>
<td>3000</td>
<td>6300</td>
<td>19</td>
<td>1.38</td>
</tr>
<tr>
<td>MM-7</td>
<td>NB-PDMAEA-C6-I$_{19}$</td>
<td>2500</td>
<td>7200</td>
<td>19</td>
<td>1.43</td>
</tr>
<tr>
<td>MM-8</td>
<td>NB-PDMAEA-C12-Br$_{19}$</td>
<td>4400</td>
<td>8000</td>
<td>19</td>
<td>1.28</td>
</tr>
<tr>
<td>MM-9</td>
<td>PDMAEA$_{24}$ $[^e]$</td>
<td>1800</td>
<td>3800</td>
<td>24</td>
<td>1.75</td>
</tr>
<tr>
<td>MM-10</td>
<td>PDMAEA-C6-Br$_{24}$ $[^e]$</td>
<td>2200</td>
<td>7800</td>
<td>24</td>
<td>1.85</td>
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<tr>
<td>MM-11</td>
<td>PDMAEA-C6-I$_{24}$ $[^e]$</td>
<td>2500</td>
<td>8900</td>
<td>24</td>
<td>1.59</td>
</tr>
</tbody>
</table>

$[^a]$ Tertiary amine MMs of NB-PDMAEA$_p$ where ‘p’ indicates DP of MM calculated from $^1$H-NMR spectra and quaternary ammonium MMs of NB-PDMAEA-C#-$X_p$ where # indicates the number of carbons in alkyl chain off the ammonium groups in repeat unit, X refers to the halide counter ions, and ‘p’ indicates MM DP calculated from $^1$H-NMR spectra. $[^b]$ Measured by SEC in DMF with 0.5 wt% LiBr as the mobile phase and linear polystyrene standards with a refractive index detector. $[^c]$ Calculated using the DP found from $^1$H NMR spectroscopy and including RAFT end-group (DP x MW of DMAEA monomer) + MW of NB-RAFT CTA for NB-PDMAEA$_p$, (DP x MW of functionalized amines including halide counter ions) + MW of NB-RAFT CTA for NB-PDMAEA-C#-$X_p$, and (DP x MW of functionalized amines including halide counter ions) + MW of DDMAT CTA for PDMAEA-C#-$X_p$. $[^d]$ Degree of polymerization calculated from $^1$H NMR end group analysis. $[^e]$ Tertiary amine polymer and quaternary ammonium polymers without norbornene end groups.
3.3.3. ROMP of quaternary ammonium macromonomers

Cationic bottlebrush homopolymers were prepared through ROMP by the grafting-through method and utilizing the high active Grubbs third-generation catalyst (G3) as an initiator in deoxygenated DCM, which was the common solvent used in ROMP due to high dielectric constant and non-coordinating with ruthenium complexes. The charge-dense MMs and the resultant cationic bottlebrush polymers were homogeneously soluble in DCM throughout ROMP. ROMP of quaternary ammonium MMs was performed with a ratio of MM to G3 as MM:G3 of 50:1 in a glove bag under nitrogen atmosphere. The reaction crudes were taken out to monitor the kinetic study and controlled characteristics at different reaction time and quenched in ethyl vinyl ether solution. $^1$H-NMR spectra showed reducing norbornene olefin intensity at 6.09 ppm as ROMP proceeded, indicating the conversion of the cyclic norbornenes to the unsaturated backbone of the polymer chains. Since qualitative end group analysis for determining MM
conversion of large bottlebrush polymers was challenging due to barely observation of an end group in the \(^1\)H-NMR spectrum, MM conversion was calculated from the relative integration of norbornene olefin peak (6.09 ppm) to methylene protons in the repeat units (4.76 ppm) that were assumed to not shift significantly during polymerization (Figure 3.12). The SEC traces suggested controlled ROMP with unimodal peaks of resulting bottlebrush polymers shifting clearly to shorter elution time, and the peak intensity of MMs reduced over time, indicating MM consumption into polymer growth, with low \(D\) values of 1.10 – 1.30 (Figure 3.13A).

Figure 3.12. \(^1\)H-NMR spectrum of crude sample of a bottlebrush homopolymer of PDMAEA-C6-Br\(_{14}\) at 53 minutes from bottlebrush polymerization of NB-PDMAEA-C6-Br\(_{14}\) MM with ratio of MM:G of 50:1 via ROMP in DCM.
Figure 3.13. Kinetic profiles of triplicate experiments of cationic bottlebrush homopolymerization of NB-PDMAEA-C6-Br14 and NB-PDMAEA-C6-I14 in DCM via ROMP (MM:G3 of 50:1, [MM]₀ = 0.03 M and [G3]₀ = 5.73 x 10⁻⁴ M). Crude aliquots were taken at different times to be analyzed by ¹H-NMR spectroscopy and SEC to obtain % MM conversion, Mₙ, and D. A) SEC traces of crude aliquots at different reaction times for the bottlebrush ROMP of NB-PDMAEA-C6-Br14 (SEC curves of ROMP of PDMAEA-C6-I14 shown in Figure S18b). B) % conversion as a function of polymerization time. C) ln([M]₀/[M]) as a function of polymerization time, assuming pseudo-first order kinetics where lines are linear fits of the data. D) Mₙ and D as a function of % conversion where lines are linear fits of the data. Error bars indicate standard deviation (n = 3).

To probe the controlled polymerization of the novel polymers, the kinetic behaviors of macromonomer ROMP have been widely studied with a variety of functional groups in the macromonomer. The reactions usually follow pseudo first-order kinetics in monomer to generate linear relationships between ln([M]₀/[M]) versus time and Mₙ as a function of % conversion. Apparent rate constant (kₚₚ) can be obtained from the slope of linear relationship between ln([M]₀/[M]) against time with constant [catalyst]₀. The kinetic profile for the bottlebrush polymerization of NB-PDMAEA-C6-Br14 deviated from this behavior as demonstrated by the large
jump in initial conversion (Figure 3.13b, black dots), by the nonlinear behavior when the conversion data was transformed (Figure 3.13c, black dots). These results suggest that the propagating center activity changed during ROMP. Interestingly, the $M_n$ increased linearly with % conversion demonstrating that the number of propagating chains did not change, proportionally consumed MMs into the polymers (Figure 3.13d, black dots). Although the MW measured by SEC used a calibration from linear polystyrene standards, which intrinsically will have different hydrodynamic behaviors compared to the brush cationic polymers, the linear behavior is consistent with controlled polymerization. Such a result suggests that the non-first order behavior of the polymerization was not a result of irreversible termination, but instead due to a change in the activity of the propagating center.

Ligand environments around the ruthenium metal center plays a role in metathesis activity of the catalyst. Halide ligand types can improve the initiation rate constant ($k_i$) by exchanging chloride ligand for bromide or iodide ligands; however, this exchange decreases the propagation rate constant ($k_p$) of the given catalyst initiator.\textsuperscript{104} Sanford et al. reported that ruthenium complexes with iodide ligands slowed the propagation rate in olefin metathesis due to the larger iodine increasing the steric effect around the ruthenium center.\textsuperscript{116} David et al. revealed that Halide ligand exchange has been observed during synthesis of cationic polymers from cationic exo-7-norbornene derivatives using the first-generation Grubbs catalyst for ROMP. Cationic monomers with bromide counter ions polymerized slower than their chloride counterparts but had a narrower MWD and still followed first-order kinetics in monomer. So, the non-first order polymerization kinetics were hypothesized to be due to halide ligand exchange between the chloride ligands of the original G3 and excess bromide counter ions from the quaternary ammonium MMs (Scheme 3.2), which would create propagating centers with zero, one, or two exchanged ligands.\textsuperscript{117,118} With this notion, ROMP of NB-PDMAEA-C6-I\textsubscript{14} ([MM]$_0$ = 0.03 M, MM:G3...
= 50) was conducted under the same conditions as NB-PDMAEA-C6-Br14. As hypothesized, MMs with iodide counter ions slowed ROMP (at 1 minute, 22% conversion versus 50% conversion for bromide counter ion) (Figure 3.13b). This difference strongly suggests that halide ligand exchange occurred during ROMP to reduce the propagation activity of the chain end. Kinetic evidence also showed a nonlinear relation (Figure 3.13c, red dots), but a linear increase of $M_n$ with % conversion (Figure 3.13d, red dots). The apparent rate constant of polymerization ($k_{app}$) based on a pseudo first-order reaction (Figure 3.13c and A.13) of MMs with iodide counter ions ($0.012 \text{ min}^{-1}$) was less than that with bromide counter ions ($0.032 \text{ min}^{-1}$) (Table 3.2, entries 1 and 2). This behavior supports the hypothesis that iodide ligands created a steric barrier that hindered incoming MMs to the propagating site. A linear increase in $M_n$ as the function of MM % conversion and low $D$ values demonstrated a constant number of propagating chains without catalyst termination throughout ROMP with iodide counter ions (Figure 3.13d, red dots). To further probe halide exchange, we attempted to synthesize quaternary ammonium MMs with chloride counter ions using the same methods as bromide and iodide counterparts, but incomplete quaternization or degradation of the MMs occurred. New methods to create chloride counter ion containing MMs are needed before conducting these future studies.

Scheme 3.2. Halide ligand exchange between chloride ligand of the original G3 and halide counter ions of quaternary ammonium macromonomers, generating mono-substitution or di-substitution of halide counter ions on the catalyst.
Table 3.2. ROMP of quaternary ammonium MMs with varied MM:G3.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Macromonomers</th>
<th>MM:G3&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Concentration (M)</th>
<th>k&lt;sub&gt;app&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; [min&lt;sup&gt;-1&lt;/sup&gt;]</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[G3]&lt;sub&gt;0&lt;/sub&gt;</td>
<td>[MM]&lt;sub&gt;0&lt;/sub&gt;</td>
</tr>
<tr>
<td>1</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>50:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.030</td>
</tr>
<tr>
<td>2</td>
<td>NB-PDMAEA-C6-I&lt;sub&gt;14&lt;/sub&gt;</td>
<td>50:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.030</td>
</tr>
<tr>
<td>3</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>25:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.015</td>
</tr>
<tr>
<td>4</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>74:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.040</td>
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<tr>
<td>5</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>100:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.057</td>
</tr>
<tr>
<td>6</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>25:1</td>
<td>1.146 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.030</td>
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<tr>
<td>7</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;19&lt;/sub&gt;</td>
<td>50:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.030</td>
</tr>
<tr>
<td>8</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;19&lt;/sub&gt;</td>
<td>35:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.020</td>
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<tr>
<td>9</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; with PDMAEA-C6-Br&lt;sub&gt;24&lt;/sub&gt;</td>
<td>25:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.015</td>
</tr>
<tr>
<td>10</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; with PDMAEA-C6-I&lt;sub&gt;24&lt;/sub&gt;</td>
<td>25:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.015</td>
</tr>
<tr>
<td>11</td>
<td>NB-PDMAEA-C6-Br&lt;sub&gt;14&lt;/sub&gt;</td>
<td>200:1</td>
<td>5.73 x 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0.114</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ratio of norbornene-functionalized MMs to the Grubbs catalyst (G3). <sup>b</sup>Slopes of the kinetic plot of ln([M]<sub>0</sub>/[M]) as a function of polymerization time from <sup>1</sup>H NMR data. Error is the standard error calculated from the least squared fit of the data. <sup>c</sup>Bottlebrush polymerization of NB-PDMAEA-C6-Br<sub>14</sub> with non-norbornene functionalized PDMAEA-C6-Br<sub>24</sub> with a ratio of MM:G3 of 14.5:1 to obtain [halide]<sub>0</sub> = 0.4 M from [Br']<sub>0</sub> = 0.2 M from NB-PDMAEA-C6-Br<sub>14</sub> and [Br']<sub>0</sub> = 0.2 M from PDMAEA-C6-Br<sub>24</sub>. <sup>d</sup>Bottlebrush polymerization of NB-PDMAEA-C6-Br<sub>14</sub> with non-norbornene functionalized PDMAEA-C6-I<sub>24</sub> with a ratio of MM:G3 of 14.5:1 to obtain [halide]<sub>0</sub> = 0.4 M from [Br']<sub>0</sub> = 0.2 M from NB-PDMAEA-C6-Br<sub>14</sub> and [I']<sub>0</sub> = 0.2 M from PDMAEA-C6-I<sub>24</sub>. <sup>e</sup>A kinetic study was not performed for these conditions.

Since the halide counter ions of quaternary ammonium MMs appeared to affect ROMP, their effect on bottlebrush polymerization was investigated further by utilizing the MMs with bromide counter ions from the evidence of nearly 100% MM consumption in ROMP (Figure 3.13B, black dot). A series of polymerizations of NB-PDMAEA-C6-Br<sub>14</sub> with MM:G3 of 25:1, 74:1, and

53
100:1 was conducted with \([G3]_0\) constant at 5.73 \(\times\) 10\(^{-4}\) M, which yielded higher \([\text{Br}^-]_0\) as seen in Table 3.2 (entries 3 – 5). If the bromide counter ions significantly affected the polymerization kinetics, the \(k_{\text{app}}\) was expected to decrease with an increase in MM:G3. Plotting the data assuming pseudo-first order kinetic behavior led to non-linear behavior with a non-zero intercept for all experiments (Figures 3.14A and A.14) consistent with counter ions affecting the catalyst. The pseudo first-order rate constant at MM:G3 of 25:1 was the largest and decreased as MM:G3 and therefore \([\text{Br}^-]_0\) increased. This behavior further suggested that the bromide ion concentration affected the ROMP. Significant halide ligand exchange with G3 appeared to occur within the first minute of the reaction to form the substituted ruthenium complexes.

Figure 3.14. Kinetic profile of cationic bottlebrush homopolymer of PDMAEA-C6-Br\(_{14}\) with varied ratio of MM:G3 and a constant \([G3]_0 = 5.73 \times 10^{-4}\) M in DCM. A) \(\ln([M]_0/[M])\) as the function of polymerization time, assuming pseudo-first order kinetics where lines are linear fits of the data.
B) $M_n$ as a function of % conversion where lines are linear fits of the data. C) SEC elution curves of final cationic bottlebrush homopolymers of PDMAEA-C6-Br$_{14}$ at 53 minutes and D) $M_n$ as the function of [MM]:[G3] for the cationic bottlebrush homopolymers of PDMAEA-C6-Br$_{14}$ at 84 % conversion.

To further probe how the halide concentration affected ROMP, NB-PDMAEA-C6-Br$_{14}$ was polymerized at a MM:G3 of 25:1, but with a higher [G3]$_0$ of $1.146 \times 10^{-3}$ M (Table 3.2, entry 6) so that [Br$^-$]$_0$ was the same as a MM:G3 of 50:1 (Table 3.2, entry 1). Doubling [G3]$_0$ doubled the $k_{app}$, which is expected if $k_{app}$ is simply the product of the propagation rate constant and [G3]$_0$ as theory describes (Figure A.15). Comparing the two MM:G3 equal to 25:1 experiments (Table 3.2, entries 3 and 6), the doubling of [G3]$_0$ also doubled the $k_{app}$ even though [Br$^-$]$_0$ was twice as high. These results suggest that the [Br$^-$]$_0$ values tested were sufficiently high that the majority of the ligand exchange occurred early in the polymerization such that when the data were fit to pseudo-first order kinetics, the $k_{app}$ captured the behavior from the new complexes created after the exchange. Significant ligand exchange early in the polymerization would also explain why the linearized kinetic data had non-zero intercepts because of the different and changing kinetic behavior in the first few minutes of monomer addition to the catalyst.

According to the assumption of halide ligand exchanges happening early in the first minute during ROMP, the experiment to prove such assumption was essential required. To further investigate how halide ligand exchange of the G3 catalyst influence ROMP of quaternary ammonium MMs, the G3 solution was mixed with quaternary ammonium polymers without polymerizable norbornene with either bromide and iodide counter ions to generate the ligand-substituted catalyst (Scheme 2) before initiating ROMP of NB-PDMAEA-C6-Br$_{14}$ (Scheme 3.3, Table 3.2, entries 9 and 10).
Scheme 3.3. Bottlebrush polymerization of NB-PDMAEA-C6-Br14 with the norbornene free cationic polymer with Bromide and Iodide counter ions. with a ratio of MM:G3 of 14.5:1 to obtain [halide]₀ = 0.4 M from [Br]₀ = 0.2 M from NB-PDMAEA-C6-Br₁₄ and [I or Br]₀ = 0.2 M from the non-norbornene functionalized cationic polymer.

After 1 minute of polymerization, conversion of NB-PDMAEA-C6-Br₁₄ reached 25% with PDMAEA-C6-Br₂₄ and 20% with PDMAEA-C6-I₂₄ as compared to about 60% conversion without the added halides (Table 3.2, entry 3 and Figure A.17). The kₚ values also decreased with the added halides (Figure A.17B). The significant decrease of % conversion at 1 minute (Figure A.17A) suggested that NB-PDMAEA-C6-Br₁₄ was not initiated with only the original G3, but also with a halide exchanged initiator that was less reactive than the G3. The empirical evidence of halide ligand exchange was demonstrated as ¹H-NMR spectra of G3 after mixing with either PDMAEA-C6-Br₂₄ and PDMAEA-C6-I₂₄ in DCM for 2 minute and 2 h periods. ¹H-NMR spectra of a mixture of G3 and either PDMAEA-C6-Br₂₄ or PDMAEA-C6-I₂₄ showed new benzylidene proton signals at lower chemical shifts, which confirms the ligand substitution (Figure 3.15). Within the same timeframe, iodide substituted more than bromide to generate more halide-substituted catalysts, which is consistent with the polymerization behavior. The iodide-substituted propagating centers polymerized slower than the bromide-substituted propagating centers likely due to their quicker formation and overall decreased rate of propagation as compared to the bromide and chloride containing centers (Figure 3.15B). Though the increased halide concentration from the non-polymerizable polymers slowed the polymerization rate, the SEC traces demonstrated controlled
polymerization with low $D$ value ($D = 1.1-1.3$) (Figure A.18), which is consistent with the other results that the number of propagating chain ends does not change throughout the polymerization.

Figure 3.15. $^1$H-NMR spectra of halide ligand exchange of G3 with quaternary ammonium polymers without a norbornene end group in DCM at a 0.5 molar ratio of polymer to catalyst. G3
before mixing with the quaternary ammonium polymers (red line), the mixture of G3 and the quaternary ammonium polymer after 2 minutes (green line), and the mixture of G3 and the quaternary ammonium polymers after 2 hours (blue line). A) ligand exchange of G3 with PDMAEA-C6-Br\textsubscript{24} and B) ligand exchange of G3 with PDMAEA-C6-I\textsubscript{24}.

Control over the molecular weight was not affected by the non-first order kinetics. A linear relation between increasing $M_n$ and the MM % conversion demonstrated well-defined bottlebrush polymer synthesis with low $D$ values of 1.10 - 1.30 (Figure 3.14B and A.16). Again, this linear relationship and low $D$ demonstrated that significant irreversible termination was unlikely. To confirm this behavior, the bottlebrush polymers made at different MM:G3 and after 53 minutes of polymerization were examined via SEC where the chromatograms (Figure 3.14C) showed unimodal curves of each bottlebrush polymer. A long tail at low molecular weight was observed in the polymerization of MM:G3 of 100, which may be from intramolecular chain transfer reactions or some termination during ROMP.\textsuperscript{110,119} As expected for controlled ROMP of PDMAEA-C6-Br\textsubscript{24}, the $M_n$ was linearly related to the initial MM:G3 (Figure 3.14D). At higher MM:G3 ratios (200:1), the linearity of the relationship between $M_n$ and MM:G3 deviates with the $M_n$ of the final bottlebrush 200:1 polymer being 2.4 times that of the 100:1 (Figure 3.16). This deviation was likely due to hydrodynamic volume differences between the linear calibration standard and large bottlebrush polymer or due to the death of the ruthenium centers during polymerization at high MM:G3 ratios. Overall, these results further demonstrated that even though the polymerization kinetics did not follow the expected behavior, the molecular weight followed controlled ROMP behavior and that molecular weights could be targeted.
Figure 3.16. ROMP of PDMAEA-C6-Br\textsubscript{14} with MM:G of 200:1 ([G]\textsubscript{0} = 5.73 \times 10^{-4} \text{ M} and [MM]\textsubscript{0} = 0.114 \text{ M}) in DCM. A) SEC elution curves of final cationic bottlebrush homopolymers at 83\% conversion in 2 hours. B) M\textsubscript{n} as the function of [MM]:[G] and dispersity values for the cationic bottlebrush homopolymers (the dash line was the linear line fit in data of M\textsubscript{n} as a function of [MM]:[G] of 25:1, 50:1, 74:1, and 100:1.

3.3.4. ROMP of MMs with higher molecular weights

The molecular weight of MMs can also influence bottlebrush polymer synthesis via ROMP due to steric hindrance at the ruthenium active site on the propagating chains slowing monomer addition.\textsuperscript{110,120} To explore the range of suitable quaternary ammonium MM molecular weights for well-defined bottlebrush polymerization, larger quaternary ammonium MMs (NB-PDMAEA-C6-Br\textsubscript{19} and NB-PDMAEA-C6-I\textsubscript{19} were prepared and polymerized under the same conditions as lower molecular weight MMs ([MM]\textsubscript{0} = 0.03 \text{ M} and MM:G3 = 50:1, Table 3.2 entry 7). Larger MMs significantly slowed ROMP yielding a k\textsubscript{app} of 0.014 min\textsuperscript{-1} (Figure 3.17A, and Figure A.19) and about 30\% conversion at 1 minute as compared to 48\% conversion for the shorter MM chain. Steric crowding from the longer side chains surrounding the ruthenium active center likely was the cause.\textsuperscript{86,106,110,120} However, larger MMs also increased the [Br\textsuperscript{-}]\textsubscript{0}, which could have impacted the ROMP propagation rate as well. To elucidate the dominating factor, ROMP of NB-PDMAEA-C6-
Br\textsubscript{19} with a MM:G3 of 35 (Table 3.2, entry 8) was performed to compare kinetic behavior with the smaller MM at the same [Br\textsubscript{-}]\textsubscript{0} (compare to Table 2, entry 1). As a result, the larger NB-PDMAEA-C6-Br\textsubscript{19} MM had a lower $k_{\text{app}}$ (Table 3.2, Figure A.20) than the smaller NB-PDMAEA-C6-Br\textsubscript{14} MM, confirming that the steric hindrance of the macromonomer side chain can significantly affect polymerization independent of halide concentration. The combination of steric barrier and halide exchange was most significant with the NB-PDMAEA-C6-I\textsubscript{19} MM where the % conversion only approached 20% in 10 minutes and then plateaued throughout the rest of the polymerization (Figure 3.17B, red dots). Due to changes in the catalyst activity and the apparent crowding at the active site, high molecular weight quaternary ammonium MMs may be challenging to polymerize via ROMP.

![Figure 3.17. A) % MM conversion as a function of polymerization time for the ROMP of NB-PDMAEA-C6-Br\textsubscript{14} and NB-PDMAEA-C6-Br\textsubscript{19}. B) % MM conversion as a function of polymerization time for the ROMP of NB-PDMAEA-C6-I\textsubscript{14} and NB-PDMAEA-C6-I\textsubscript{19}.

Figure 3.17. A) % MM conversion as a function of polymerization time for the ROMP of NB-PDMAEA-C6-Br\textsubscript{14} and NB-PDMAEA-C6-Br\textsubscript{19}. B) % MM conversion as a function of polymerization time for the ROMP of NB-PDMAEA-C6-I\textsubscript{14} and NB-PDMAEA-C6-I\textsubscript{19}.
time for the ROMP of NB-PDMAEA-C6-I14 and NB-PDMAEA-C6-I19. C) % MM conversion as a function of polymerization time for the ROMP of NB-PDMAEA-C12-Br14 and NB-PDMAEA-C12-Br19. D) SEC trace of aliquots from the ROMP of NB-PDMAEA-C12-Br14 as a function of reaction time. All polymerizations were run at a MM:G3 of 50:1 in DCM, [G3]₀ of 5.73 x10⁻⁴ M, and [MM]₀ = 0.03 M. Error bars indicate one standard deviation.

In addition to the MM length affecting ROMP, how the pendant alkyl group of the quaternary ammonium MM affected bottlebrush polymer synthesis was studied using quaternary ammonium MMs with bromide counter ions and 12-carbon alkyl chains ([MM]₀ = 0.03 M and MM:G3 = 50:1). The steric hindrance from the longer alkyl chains prevented high monomer consumption for both NB-PDMAEA-C12-Br14 and NB-PDMAEA-C12-Br19 MMs (Figure 3.17C) as compared to their 6-carbon counterparts. The % conversion obtained from ¹H-NMR spectroscopy reached approximately 20% at 1 minute and then slightly increased over time with corresponding changes in the SEC traces, which is indicative of a still active catalyst (Figure 3.17D). These results demonstrate that the bulky pendant alkyl groups significantly hindered the propagating center from reacting with the MMs and thus significantly reduced the propagation rate without catalyst termination. Though other macromonomers with bulky pendent groups have been polymerized through ROMP with the G3 catalyst,¹⁰¹ these results demonstrate that the changing catalytic activity throughout the polymerization due to halide exchange coupled with the steric hindrance can significantly slow ROMP.

3.3.5 Amphiphilic bottlebrush block copolymerization via ROMP

Since the controlled polymerization of NB-DMAEA-C6-Br₁₄ to varied DPs was demonstrated, amphiphilic bottlebrush block copolymerization was examined by utilizing NB-PDMAEA-C6-Br₁₄ and a polystyrene MM, NB-PS₁₇. NB-PS MMs have been widely polymerized by ROMP to yield well-defined bottlebrush block copolymers using a variety of anchor norbornene
In this work, a NB-PS MM with the same anchor group as the quaternary ammonium MMs was prepared from RAFT polymerization to obtain a 17 DP MM (2,000 g/mol). Sequential ROMP off a poly(NB-PDMAE-A-C6-Br14) was demonstrated by polymerizing NB-PS17 at MM1:MM2:G3 equal to 25:25:1 (Scheme 3.4A). From the SEC chromatogram, a unimodal, but slightly broader peak of the block copolymer (M_n of 60,000 g/mol and a D of 1.40) developed at a shorter elution time compared to the cationic macroinitiator (Figure 3.18A). The unimodal curve shift to higher molecular weight suggests complete initiation off the poly(NB-PDMAEA- C6-Br14) chain, but the broader distribution is indicative of slower initiation of the growing poly(NB-PS17) chain (see Figure A.21 for 1H-NMR spectra). These results are consistent with decreased propagating center activity due to halide exchange with the original G3 catalyst and the steric hindrance of the quaternary macroinitiator and not a polymer chain end termination mechanism.

Since we hypothesized that the quaternary ammonium macroinitiator was slowing initiation, the amphiphilic bottlebrush block copolymer was produced by polymerizing quaternary ammonium MMs off a PS macroinitiator (Scheme 3.4B). By changing the order of addition, the block copolymerization yielded a narrower dispersity (Figure 3.18B) with M_n of 73,000 g/mol and a D of 1.26 (see Figure A.22 for 1H-NMR spectra), indicating that the PS-block could efficiently initiate the quaternary ammonium MM polymerization since it was less sterically bulky and retained the original propagating center activity. These results demonstrate a new method to produce amphiphilic bottlebrush block copolymers with quaternary ammonium groups.
Scheme 3.4. Amphiphilic bottlebrush block copolymerization via grafting-through ROMP in DCM with sequential macromonomer addition at MM1:MM2:G3 of 25:25:1. ([G3]₀ = 5.73 x 10⁻⁴ M, [MM1]₀ = 0.015 M, and [MM2]₀ = 0.011). A) PDMAEA-C6-Br₁₄-a and B) PS₁₇-b-PDMAEA-C6-Br₁₄.

Figure 3.18. SEC traces of amphiphilic bottlebrush block copolymerization via ROMP in DCM with MM1:MM2:G3 of 25:25:1 ([G3]₀ = 5.73 x 10⁻⁴ M, [MM1]₀ = 0.015 M, and [MM2]₀ = 0.011 M.) A) First polymerizing NB-PDMAEA-C6-Br₁₄ (black curve) with subsequent NB-PS₁₇ MM addition, yielding a block copolymer (red curve). B) First polymerizing NB-PS₁₇ (black curve) with subsequent NB-PDMAEA-C6-Br₁₄ MM addition, yielding a block copolymer (red curve).
3.4 Conclusions

A facile procedure to synthesize full density quaternary ammonium bottlebrush polymers by a grafting-through ROMP technique was realized to generate well-defined molecular brushes. A library of quaternary ammonium MMs could be prepared from tertiary amine MMs by quaternizing with bromo- and iodo-alkanes. During ROMP, halide ligand exchange between chloride ligands of the original G3 catalyst and halide counter ions of cationic MMs occurred, which changed the propagating center activity as evidenced by MMs with iodide counter ions polymerizing slower than those with bromide counter ions. Larger quaternary ammonium MMs and larger pendent alkyl groups reduced the rate of polymerization and could even stop polymerization due to these groups likely crowding around the propagating center. Lower MW of MMs with six-carbon alkyl chains afforded well-defined bottlebrush polymers with dispersity below 1.30 and nearly complete monomer conversion. Kinetic profiles of quaternary ammonium MM homopolymerization deviated from pseudo-first-order kinetic behavior due to changing propagating center activity, but still followed controlled polymerization with desired MW and low dispersity. Despite changing propagating center activity during ROMP, sequential ROMP of NB-PDMAEA-C6-Br and NB-PS could yield block copolymers where those polymerized with NB-PS first yielded the lowest dispersity. By demonstrating methods to produce well-defined quaternary ammonium bottlebrush polymers and amphiphilic bottlebrush block copolymers, libraries of materials can be synthesized to explore their antibacterial and phase separation properties in the future.
CHAPTER 4

AMPHIPHILIC BOTTLEBRUSH BLOCK COPOLYMERIZATION BY RING OPENING METATHESIS POLYMERIZATION (ROMP) AND NANOSTRUCTURED SELF-ASSEMBLED THIN FILMS

4.1 Introduction

4.1. Block copolymers

Block copolymers are a macromolecule containing two or more immiscible polymers connected with chemical bonds. The immiscibility of distinct blocks and chemical linkage drive phase separation into nanostructures. Block copolymers (BCPs) have attracted considerable attention due to their self-assembly into nanostructures,\(^\text{121,122}\) leading to various useful applications as drug carriers,\(^\text{88}\) stimuli-responsive materials,\(^\text{123}\) ion exchange membranes,\(^\text{124}\) and anti-biofouling coatings.\(^\text{125,126}\) Block copolymers can be generated in various architectures: linear diblock and triblock copolymers, a bottlebrush block structures, a star block shape, or a cyclic block structure, depending on advanced synthesis techniques (Figure 4.1).\(^\text{127}\)

![Figure 4.1. A variety of architectures of block copolymers.](image-url)
4.1.1 Self-assembly of block copolymers

The main contributions influencing phase separation are the interfacial energy between two blocks and chain stretching of the polymers. In other words, the optimization between enthalpy and entropy contributions plays a significant role in the process of phase segregation.\textsuperscript{128} The self-assembly process of BCPs is associated with minimization of contact between each domain under the constraint of covalent linkages in single polymer molecule, while the polymer stretches out to individual distinct segments, avoiding a preferred coil polymer chain conformation. In bulk, as phase segregation occurs, the adopted phases in an ordered system can be varied depending on the compositions of each block relative to one another. For example, an AB diblock (A-b-B) with a significantly minor A segment will orient the A polymers into spherical domains, while the majority of B block will act as a matrix. As an A block increases proportionally to decreasing B domains, a new morphological feature forms, called a cylindrical morphology, which originates from reduced interfacial curvature and polymer chain stretching. Once the A and B composition are symmetrical, the flat sheet is packed layer by layer, which is well-known as a lamellar conformation (Figure 4.2).\textsuperscript{129}
Figure 4.2. Schematic illustration of self-separation of AB block copolymer into varied morphologies primarily depending on the composition of each block relative to one another in a copolymer chain. A) The cone-column mechanism of A-b-B polymer of which the black domains belong to A blocks that contains small volume fraction ($f$) and then rising to 0.5, whereas red areas belong to B segments, and black dash line indicated. B) Equilibrium morphology transitions of phase segregation started from sphere, cylinder, lamellar, inverse cylinder, and inverse sphere.

The self-assembly of BCPs minimizes contact between each domain, generating phase behaviors that can be tuned by volume fraction ($f$), total degree of polymerization ($N$), and the Flory-Huggins interaction parameter ($\chi$). Linear BCPs with chemically incompatible blocks can spontaneously phase segregate into 10 - 40 nm domains from polymers with molecular weights (MWs) of 10-100 kg/mol. Creating larger domains (>100nm) from linear BCPs is challenging due to difficult polymer synthesis and high chain entanglement making phase separation challenging. Unlike linear BCPs, bottlebrush block copolymers (BBCPs) overcome these limitations to afford large nanodomains since the intrinsic repulsive interaction between densely packed side chains stretches out the polymer backbone to hinder chain entanglement,
subsequently facilitating phase separation.\textsuperscript{134} Although a common morphology of BBCPs is lamella, other structures are possible through varying block composition and side chain asymmetry in the blocks.\textsuperscript{95,135,136} These morphologies can behave differently when BBCPs are in thin films. Thus, understanding the molecular structure factors that influence BBCPs surface morphologies is needed for surface applications.

BBCP phase behaviors can be different than those from linear BCPs or comb-like polymers since the dense polymer side chains grafted-off the molecular backbone extend the polymer chain, thereby yielding a shape-persistent macromolecule.\textsuperscript{135,137} Additional factors like volume fraction asymmetry, branch asymmetry, and length of the polymer backbone also play a crucial role in manipulating BBCP phase separated morphologies and domain spacing because they directly affect the molecular packing and interfacial curvature during self-assembly.\textsuperscript{137,138} Interfacial curvatures become small for BBCPs with symmetric side chains, while they are higher for BBCPs with asymmetric side chain lengths in the blocks.\textsuperscript{139,137} Thus, BBCPs have drawn attention to be utilized as cargo carriers in water\textsuperscript{140} and solid state applications.\textsuperscript{114,141,142}

BBCP films have employed for antimicrobial applications\textsuperscript{38,39} and the prevalent functional groups used in this field are quaternary ammonium groups.\textsuperscript{143} The electrostatic interaction between quaternary ammonium groups and negative charges of bacteria’s cell wall can lead to cell rupture and cell death. The direct synthesis of well-defined amphiphilic block copolymers carrying cationic functional groups is challenging due solvent selection to keep both blocks soluble. An alternative method is to do the post-modification of precursor block copolymers to yield polymers with the charged blocks; however, this process can lead to incomplete modification.\textsuperscript{144,145,146} Although direct creation of BBCPs with a high density of charged constituents in the polymer chains is challenging, our recent publication reported the first
successful methodology to synthesize well-defined BBCPs by grafting-through approach, yielding a dense charge-based macromolecular brush.\textsuperscript{147}

Herein, we report a technique to synthesize amphiphilic BBCPs containing dense side chains of quaternary ammonium groups by grafting-through ring opening metathesis polymerization (ROMP). As briefly demonstrated in a previous publication,\textsuperscript{147} sequential ROMP of norbornene-capped polystyrene macromonomers (PS-MM) and then norbornene-functionalized quaternary ammonium macromonomers with six-carbon pendant groups afforded well-defined amphiphilic BBCPs with low dispersity (Scheme 4.1). A library of these BBCPs was synthesized to explore the thin-film phase behaviors by atomic force microscopy (AFM) for different volume fractions, symmetries of side chains, and total degrees of polymerization. Last, the stability of morphologies was examined upon water exposure. Understanding the nanometer-scale phase behaviors of these polymers widen opportunities for developing potential candidates for antifouling materials and other applications where cationic charges are important.

Scheme 4.1. Amphiphilic cationic bottlebrush block copolymerization by sequential ROMP of polystyrene MMs (NB-PS) and quaternary ammonium MMs (NB-PDMH)
4.2 Experimental details

4.2.1 Materials

All chemicals and solvents were purchased from commercial sources and used as received unless otherwise noted. Inhibitors were removed from styrene (St) and 2-(dimethylamino)ethyl acrylate (DMAEA) by passing through a basic alumina column and vacuum distillation prior to use, respectively. Inhibitor free anhydrous tetrahydrofuran (THF), ACS grade methylene chloride (DCM), and ethyl vinyl ether (EVE) was used as received. The third generation Grubbs catalyst, \((\text{H}_2\text{IMes-pyr})_2\text{Cl}_2\text{RuCHPh} \) (G3), polystyrene (NB-PS) with degree of polymerizations (DPs) of 17 and 39 and norbornene-functionalized poly(dimethylhexyl bromo)ethyl acrylate (NB-PDMH) with a DP of 14 were synthesized according to previously reported procedure.\(^{147}\)

4.2.2. Characterization

4.2.2.1. Size Exclusion Chromatography (SEC)

Number average molecular weight \((M_n)\) and dispersity values \((\mathcal{D})\) were obtained from size exclusion chromatography (SEC) analysis using 1260 Agilent module, three Phenogel (Phenomenex) columns in series with pore sizes 50, \(10^3\), and \(10^6\) Å, and a refractive index detector with linear polystyrene standards. SEC analysis was performed using a mobile phase of dimethylformamide (DMF) containing 0.5 wt\% LiBr salt, filtered through 0.45 µm polypropylene (PP) membrane before use, with the flow rate 1.0 mL min\(^{-1}\) at 70 °C.

4.2.2.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

\(^1\text{H}-\text{NMR}\) spectra were obtained from using a Bruker Avance NEO 500 MHz spectrometer in deuterated chloroform (CDCl\(_3\)).
4.2.2.3. Differential Scanning Calorimetry (DSC).

DSC was performed on a TA Instruments 2500 to determine the glass transition temperature ($T_g$) of the bottlebrush polymers. Approximately 2.0 mg samples were heated under nitrogen atmosphere over a temperature range of 0 to 160 °C at a ramp rate of 10 °C/min using a heat/cool/heat cycle. The $T_g$ was reported from the second heating data.

4.2.2.4. Water contact angle measurements.

Water contact angles were measured with a Mobile Surface Analyzer (Krüss) by using 1 μL droplet of water at 20 °C. Prior to measurement, the water droplet was equilibrated on the polymer thin films for 60 seconds. The reported data were derived from 6 analyzed spots of 2 replicate samples and then averaged using the measured angles from the left and the right side of the droplet.

4.2.2.5. Atomic force microscopy (AFM).

AFM was performed to analyze the surface topographies (height images) and morphologies (phase images) of the polymer films through tapping mode, using silicon cantilevers (model of AC160TS-R3 received from OXFORD instruments) with a resonant frequency of 300 kHz, spring constant of 26 N/m, and a silicon tip radius of 7 nm. All images over regions of 2 x 2 μm$^2$ were analyzed by running a set amplitude at 25% of a drive amplitude with a 0.5 Hz scan rate and 192 scan points and lines. The polymer films were kept under vacuum prior to AFM characterization. Domain spacings (d-spacing) were determined by computing the phase images in Gwyddion software (version 2.54) through a radial power spectral density function (radial PSDF) to provide plot of the radial average in terms of intensity (y-axis) versus distance (nm$^{-1}$). Then, the plot was fit by a Lorentzian function to provide a q-value as the maximum intensity of the fit curve.
The q-values were used in equation 1 to evaluate the domain spacing \((L_0, \text{nm-scale})\) of the phase separated BBCPs.\(^{144}\) The domain spacing was measured for four different AFM phase images over regions over \(2 \times 2 \mu \text{m}^2\) and averaged to provide average domain spacing values and standard deviation. The root-mean square of the surface roughness \((R_{\text{rms}})\) was determined from AFM height images through the equation 2 of which \(m\) and \(n\) were the number of points measured on the analyzed surface, \(Z\) was the height, and \(x, y\) was the a in-plane coordinate in the AFM software.

\[
L_0 = \frac{2\pi}{q} \quad (\text{Equation 4.1})
\]

\[
R_{\text{rms}} = \sqrt{\frac{1}{mn} \sum_{j=1}^{n} \sum_{i=1}^{m} Z^2(x_i, y_j)} \quad (\text{Equation 4.2})
\]

4.2.3. Synthetic methods

4.2.3.1. Synthesis of polystyrene macromonomer by RAFT polymerization with DP of 39, NB-PS\(_{39}\).

The mixture of purified styrene monomer (St), NB-RAFT CTA, and AIBN was prepared with a ratio of St to NB-RAFT CTA to initiator as 400:1:0.05 in a 250 mL Schlenk round bottom flask equipped with a stir bar. The yellow mixture was degassed by three freeze-pump-thaw cycles and then heated in the preheated oil bath at 52 °C for 3 h. The reaction was quenched by putting the flask in ice bath for 30 minutes. To work up, the unreacted St monomers were eliminated by multiple precipitation from THF to dry ice-chilled methanol until no trace of St monomer observed in \(^1\text{H}-\text{NMR}\) spectrum. The purified solid PS was dried in vacuum oven at room temperature to dry out the solvent. Monomer conversion was determined from \(^1\text{H}-\text{NMR}\) spectrum by end group analysis, using a norbornene peak at 6.07 ppm and styrene repeat units in range of 6.20 -7.20
ppm, and the polymerization characteristic was examined by SEC. As a result, the % conversion from end group analysis was 10% to generate NB-PS with DP of 39 and $M_n$ was 4000 g/mol and low $D$ was 1.29. The polymer was referred to NB-PS$_{39}$.

4.2.3.2. Synthesis of amphiphilic bottlebrush block copolymers of PS-b-PDMH by ROMP

In a general procedure for amphiphilic bottlebrush block polymerization via ROMP, all vials, stir bars, and syringes were dried before use and ROMP was undertaken in a glove bag under N$_2$ atmosphere. The desired amount of NB-PS and NB-PDMH macromonomers (MMs) were prepared in separate 4 mL vials equipped with a stir bar and rubber septa cap and then purged with nitrogen gas for 30 minutes. A 20 mL ampule with 10 mL DCM was degassed by three freeze-pump-thaw cycles prior use. In an experimental example for ROMP of PS$_{17}$-b-PDMH with NB-PS$_{17}$:NB-PDMH:G3 of 50:50:1, in a glove bag 0.28 mL of DCM was added to the individual vials to prepare the 0.05 M MM solution using an airtight glass syringe. Then, 0.2 mL of freshly prepared G3 solution (1 mg/mL in DCM, 0.0002 g, $2.75 \times 10^{-4}$ mmol) were added to the vial containing NB-PS solution to start Homopolymerization, which ran for 6 minutes. After this time, an aliquot of the crude of bottlebrush polystyrene was extracted and then quenched with an 0.3 mL EVE in 0.6 mL DCM (33% v/v). The NB-PDMH MM solution was sequentially added into the remaining bottlebrush polystyrene solution by a N$_2$-purged syringe to continue block copolymerization, which was run for 2 h. ROMP reactions were quenched by adding 0.3 mL EVE in 0.6 mL DCM (33% v/v) to the reaction vial. All crude samples were purged with N$_2$ gas to eliminate excess EVE then dried in a vacuum oven at 45 °C for 2 days to remove the remaining EVE before being analyzed by $^1$H-NMR spectroscopy in CDCl$_3$ and SEC to find % MM conversion, $M_n$, and dispersity. For other polymerizations, the same procedures were performed at the same concentrations of MM and G3 solutions by using the amount of starting materials corresponding to the desired ratios of NB-PS to NB-PDMH to G3. Polymerizations were run to achieve at least 95 % conversion of NB-PDMH.
The block copolymers were purified by precipitation into dry-ice chilled diethyl ether from DCM twice and then precipitated into dry-ice chilled diethyl ether from chloroform twice. The precipitate in diethyl ether was collected by centrifugation and then dried in a vacuum oven.

4.2.3.3. Preparation of polymer films.

Glass slides were cleaned by immersion and sonication in a sequence of solvents: reverse osmosis water (RO water), acetone, and isopropanol for 1 hour and then dried in vacuum oven overnight. BBCP solutions were prepared in chloroform (CHCl₃) at a 20 mg/mL concentration by stirring for 30 minutes before being filtered through a 0.20 µm syringe filter. The filtered polymer solutions (100 µL solution) were spin-coated onto the cleaned glass slides with the spin rate of 1500 rpm for 30 seconds and then 500 rpm for additional 30 seconds. For the thermal treatment of the films, after the BBCP solutions were spin-coated, the freshly made films were thermally annealed in a vacuum oven at 110 °C for 17 h. Then, the films were kept under vacuum prior to AFM characterization.

4.2.3.4. Water submersion of BBCP thin films.

BBCP thin films were submerged in reverse osmosis (RO) water for 3 immersion cycles. For the first cycle of film submersion, the films were immersed under water for 3 hr and transferred to dry in a vacuum oven at room temperature for 18 hr. Then, films were analyzed by AFM. After, the films were submersed under RO water for another 3 hr (total submersion period was 6 hr), dried in vacuum oven for 18 hr, and further analyzed by AFM. Last, the films were submerged for 3 days, dried in the vacuum oven for 10 days and analyzed by AFM.

4.4.3.5. Measurement of polymer thickness on thin film.
The polymer thin films of PS-b-PDMH were prepared by attaching 3 strips of invisible tape with approximately 1 mm width on a clean glass slide. Then, 20 mg/mL BBCP solutions (100 µL solution) were spin-coated onto the modified glass slides with the spin rate of 1500 rpm for 30 seconds and then 500 rpm for additional 30 seconds. The polymer-coated glass slides were dried under vacuum for 17 h. The tapes were peeled off to provide the polymer-free regions underneath the attached tapes prior to AFM analysis. The topographies of the films were characterized over the rectangular regions of 2 x 20 µm² (Figure 4.3). The coating thicknesses were measured by the cross-section method across the polymer and polymer-free regions (Figure B.11).

Figure 4.3. Schematic for the polymer film preparation to measure coating thickness.

4.3. Results and Discussion

4.3.1. BBCPs synthesis of PS-b-PDMH and characterization

Amphiphilic bottlebrush block copolymerization was carried out by sequential grafting-through ROMP of norbornene-functionalized MMs with a highly active third generation Grubbs catalyst (G3) in deoxygenated DCM. This powerful technique ensured dense side chains on every repeat unit and generated architectures with controlled degrees of polymerization (DPs). Prior to ROMP, MMs of NB-PS and NB-PDMH were prepared through reversible addition-fragmentation
chain transfer (RAFT) polymerization by using a chain transfer agent with a norbornene terminus (NB-RAFT CTA), and subsequent quaternization with 1-bromohexane to create NB-PDMH. $^1$H-NMR spectra showed that the resulting NB-PS$_{17}$ (17 DP), NB-PS$_{39}$ (39 DP), and NB-PDMH (14 DP) MMs could be synthesized with norbornene end groups (Figure 4.4). Two NB-PS were synthesized to probe how symmetry of the side chain lengths affected the self-assembled morphology. SEC analysis demonstrated unimodal curves for all resulting MMs with dispersity ($\mathcal{D}$) below 1.3, suggesting controlled macromonomer structures were produced (Figure 4.5A and Table B.1).

As previously reported, sequential polymerization of NB-PS and NB-PDMH MMs afforded well-defined architectures of BBCPs with low $\mathcal{D}$. A library of BBCPs was generated by tuning the feed ratios of NB-PS to NB-PDMH to G3 (NB-PS:NB-PDMH:G3) as summarized in Table 4.1. $^1$H-NMR spectra showed successful ROMP of PS$_{17}$-b-PDMH as evidenced of disappearance of the norbornenyl olefin peak (NB) at 6.07 ppm and the generation of vinyl peaks at 4.9 – 5.5 ppm, corresponding to the formed polynorbornene backbone (Figure 4.4). This indicates an efficient initiation of PS macroinitiators with the ruthenium reactive site to further polymerize NB-PDMH by quantitative MM consumption. The $^1$H-NMR spectrum of the precipitated BBCPs proved successful sequential ROMP by incorporation of PS and cationic side chains into the macromolecular chain (Figure 4.4). In this study, all crude of BBCPs were polymerized to higher that 95% MM conversion and were then precipitated to eliminate unreacted MMs, yielding BBCPs with less than 3% impurities, which should likely not significantly impact surface morphologies.
Figure 4.4. $^1$H-NMR spectra of norbornene-functionalized quaternary ammonium MM of NB-PDMH (14 DP), norbornene-functionalized polystyrene of NB-PS$_{17}$ (17 DP), and precipitated BBCP of PS$_{17}$-b-PDMH with DP molar ratio for PS:NB-PDMH:G3 of 200:100:1.
Table 4.1. BBCPs of PS-b-PDMH synthesized by sequential ROMP.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>[NB-PS]₀: [NB-PDMH]₀ : [G3]₀</th>
<th>% Conversion (^a)</th>
<th>(M_n(\text{SEC})) (kg/mol) (^b)</th>
<th>(D) (^b)</th>
<th>DP of PS:PDMH (^c)</th>
<th>(f_{\text{PDMH}}) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>25:25:1</td>
<td>96</td>
<td>78</td>
<td>1.25</td>
<td>25:24</td>
<td>0.73</td>
</tr>
<tr>
<td>2</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>50:25:1</td>
<td>&gt;99</td>
<td>120</td>
<td>1.16</td>
<td>50:25</td>
<td>0.58</td>
</tr>
<tr>
<td>3</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>50:50:1</td>
<td>97</td>
<td>145</td>
<td>1.24</td>
<td>50:48</td>
<td>0.73</td>
</tr>
<tr>
<td>4</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>100:50:1</td>
<td>97</td>
<td>160</td>
<td>1.20</td>
<td>100:49</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>100:100:1</td>
<td>98</td>
<td>210</td>
<td>1.23</td>
<td>100:98</td>
<td>0.73</td>
</tr>
<tr>
<td>6</td>
<td>PS₁₇₋₁₋b-PDMH</td>
<td>200:100:1</td>
<td>&gt;99</td>
<td>230</td>
<td>1.33</td>
<td>200:100</td>
<td>0.58</td>
</tr>
<tr>
<td>7</td>
<td>PS₂₉₋₁₋b-PDMH</td>
<td>200:200:1</td>
<td>90</td>
<td>270</td>
<td>1.63</td>
<td>200:180</td>
<td>0.73</td>
</tr>
<tr>
<td>8</td>
<td>PS₂₉₋₁₋b-PDMH</td>
<td>50:100:1</td>
<td>&gt;99</td>
<td>190</td>
<td>1.29</td>
<td>50:100</td>
<td>0.71</td>
</tr>
<tr>
<td>9</td>
<td>PS₂₉₋₁₋b-PDMH</td>
<td>100:50:1</td>
<td>&gt;99</td>
<td>250</td>
<td>1.25</td>
<td>100:50</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>PS₂₉₋₁₋b-PDMH</td>
<td>100:100:1</td>
<td>&gt;99</td>
<td>230</td>
<td>1.48</td>
<td>100:100</td>
<td>0.55</td>
</tr>
</tbody>
</table>

\(^a\) % NB-PDMH conversion calculated from \(^1\)H-NMR spectroscopy in CDCl₃ from the relative integration of methylene protons at 4.76 ppm in the repeat units to norbornene protons at 6.09 ppm. \(^b\) Obtained from SEC analysis in DMF with 0.5 wt% LiBr, RI detector, and linear PS standards. \(^c\) Determined from % NB-PDMH conversion x feed ratios of [NB-PS]₀:[NB-PDMH]₀:[G3]₀, with 100 % conversion of NB-PS₁₇ or NB-PS₃₉. \(^d\) Measured from equation of \(f_{\text{PDMH}} = V_{\text{PDMH}}/(V_{\text{PDMH}}+V_{\text{PS}})\) and using density of PDMH as 0.915 g/mL and density of PS as 1.04 g/mL, where \(V_{\text{PDMH}}\) and \(V_{\text{PS}}\) are defined as volume per mole of a polymer chain of PDMH and PS, respectively (The calculation expression was shown in appendix B.12).

SEC chromatograms exhibited unimodal curves of the BBCPs clearly shifting to shorter elution time, higher MW regions, as compared to the NB-PS macroinitiator with \(D\) below 1.3, suggesting efficient PS-based initiation to yield well-structured BBCPs (Figure 4.5B – 4.5C). Larger BBCPs with higher \(M_n\) were prepared by varying the feed ratio of NB-PS:NB-PDMH:G3 and generally produced low dispersity BBCPs. However, the BBCP with the highest feed ratio of NB-PS₁₇ to NB-PDMH to G3 (200:200:1) showed a broader molecular distribution with a shoulder at higher MW and a \(D\) of 1.63 (Figure 4.5C, yellow dash line). This shoulder was likely due to intermolecular chain transfer reactions caused by the highly viscous reaction solution. Larger arm PS brushes (PS₃₉) also efficiently acted as macroinitiators as demonstrated by unimodal peaks of
the resulting BBCPs and low $D$ (Figure 4.5D). A library of well-defined amphiphilic BBCPs were synthesized using this method to investigate phase segregation as summarized in Table 4.1.

Figure 4.5. SEC elution curves of norbornene-functionalized MMs and BBCPs synthesized with varied feed ratios of NB-PS:NB-PDMH:G3. A) SEC curves of norbornene-functionalized MMs: NB-PS$_{17}$ (17 DP), NB-PS$_{39}$ (39 DP), and quaternary ammonium MMs of NB-PDMH (14 DP). B) SEC curves of BBCPs of PS$_{17}$-b-PDMH from NB-PS$_{17}$ macroinitiators with ratios of NB-PS$_{17}$:G3 of 100:1 referred to as PS$_{17}$ 100:1. C) SEC curve of BBCPs of PS$_{17}$-b-PDMH from NB-PS$_{17}$ macroinitiators with ratios of NB-PS$_{17}$:G3 of 200:1 referred to as PS$_{17}$ 200:1. D) SEC curve of BBCPs of PS$_{39}$-b-PDMH from NB-PS$_{39}$ macroinitiators with ratios of NB-PS$_{39}$:G3 of 100:1 referred to as PS$_{39}$ 100:1.
4.3.2. Differential Scanning Calorimetry (DSC) of bottlebrush polymers.

The glass transition temperature ($T_g$) of bottlebrush homopolymers of NB-PS$_{17}$ and NB-PDMH with a DP of 100 were determined by DSC to be 69 °C and 34 °C, respectively (Figure 4.6). The DSC data for BBCPs of PS$_{39}$-b-PDMH with DPs of 100 and 100 for each block demonstrated a qualitative indication that the immiscible polymers phase separated as evidenced by two separate $T_g$ values corresponding to PS and PDMH (Figure 4.6). However, the DSC results of PS$_{17}$-b-PDMH with same backbone DPs as PS$_{39}$-b-PDMH (100 and 100) revealed one broad $T_g$ value at 47 °C, suggesting less well-defined regions of the dissimilar polymers (Figure 4.6). This result suggests that the shorter PS side chains tend to interact more with the hydrophobic six-carbon alkyl chains off the quaternary ammonium functional groups in the branches as compared to the longer side chain PS$_{39}$.

![DSC thermograms](image)

**Figure 4.6.** DSC thermograms of precipitated bottle brush polymers of PPS$_{17}$ and PPDMH with DP of 100 and precipitated amphiphilic bottlebrush block copolymers of PS$_{39}$-b-PDMH and PS$_{17}$-b-PDMH with DP of PS:PPDMH:G3 of 100:100:1.
4.3.3. BBCP thin film self-assembly behavior

All BBCP thin films were prepared by spin-casting from chloroform (CHCl₃) and then drying under vacuum to remove residual CHCl₃. Since the method of film preparation can impact phase separation of the BBCPs due to polymer-substrate interactions, polymer-atmosphere interactions, and drying rates, drying under vacuum was used to provide consistency. The coatings prepared from BBCPs with various \( f_{\text{PDMM}} \), overall DP, and symmetry of block side chain length were characterized by AFM to explore phase separation and resultant morphology (Figure 4.7A). AFM phase images confirmed self-assembly of PS and PDMH domains as evidenced by the distinct phase contrast on the surfaces (Figure 4.8). Morphological changes for PS₁₇-b-PDMH films were observed as \( f_{\text{PDMM}} \) increased from about 0.58 to about 0.73, influencing molecular packing shapes and interfacial curvatures (Figure 4.8 top and middle rows and Figure B.1A and B.2A). AFM phase images of the films with \( f_{\text{PDMM}} \) of 0.73 and higher DP showed enrichment of the bright domain on the surface, suggesting that bright areas were the PDMH regions and dark areas were the PS segments (Figure 4.8 middle row).¹⁴⁴ With the asymmetric side chain lengths of PS₃₉ (DP of 39) and PDMH (DP of 14), phase behaviors revealed more circular morphology on the surface, demonstrating more curved interfaces between the domains of each block¹³⁹ (Figure 4.7B and Figure 4.8, bottom row, and Figure B.3A). Morphological transitions for PS₃₉-based BBCPs were clearly noticeable as \( f_{\text{PDMM}} \) increased from 0.4 to 0.7 as bright domains began to elongate (Figure 4.8 bottom row). Domain spacing (\( L_0 \)) determination carried out on the AFM phase images of all coatings demonstrated larger \( L_0 \) values with increasing DP of molecular brush backbone as expected (Table 4.2).
Figure 4.7. A) Schematic architectures of BBCPs with varied volume fraction of PDMH ($f_{PDMH}$) and different side chain lengths, yielding bottlebrushes with side chain asymmetry and symmetry for PS$_{39}$-b-PDMH and PS$_{17}$-b-PDMH, respectively. B) Representative schematic of molecular packing through interfacial curvature manipulated by asymmetry of side chain lengths and $f_{PDMH}$.

Figure 4.8. AFM phase images of PS$_{17}$-b-PDMH films (top and middle row), and PS$_{39}$-b-PDMH films (bottom row) with varied $f_{PDMH}$ and DP of PS:PDMH.
Table 4.2. Domain spacing ($L_o$) of BBCP thin films determined from AFM phase images.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[NB-PS]$_n$: [NB-PDMH]$_o$</th>
<th>$L_o$ of films before water submersion$^a$ (nm)</th>
<th>$L_o$ of films after water submersion$^a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unannealed film</td>
<td>Thermal-annealed film</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>50:25</td>
<td>62 ± 2</td>
<td>118 ± 3</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>100:50</td>
<td>91 ± 1</td>
<td>184 ± 11</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>200:100</td>
<td>111 ± 3</td>
<td>151 ± 9</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>25:25</td>
<td>50 ± 5</td>
<td>64 ± 3</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>50:50</td>
<td>115±9</td>
<td>101±4</td>
</tr>
<tr>
<td>PS$_{17}$-b-PDMH</td>
<td>100:100</td>
<td>155±2</td>
<td>146±6</td>
</tr>
<tr>
<td>PS$_{32}$-b-PDMH</td>
<td>50:100</td>
<td>94±1</td>
<td>141±2</td>
</tr>
<tr>
<td>PS$_{32}$-b-PDMH</td>
<td>100:50</td>
<td>73±2</td>
<td>183±8</td>
</tr>
<tr>
<td>PS$_{32}$-b-PDMH</td>
<td>100:100</td>
<td>117±3</td>
<td>154±12</td>
</tr>
</tbody>
</table>

$^a$Obtained from measuring four different AFM phase images over two different analyzed regions on the thin films and then reported as average ± standard deviation of four AFM phase images.

Since amphiphilic surfaces often target applications in aqueous environments, the stability of the morphology after water submersion was studied because surface structures can change due to structural reorganization of the polymer segments under water.$^{32}$ PS$_{17}$-b-PDMH films with a DP of 200:100 ($f_{PDMH} = 0.58$) and 100:100 ($f_{PDMH} = 0.73$) were submerged under water for 3-cycles. After initial water submersion, AFM height images of the films demonstrated a significant roughness increase as compared to the dry state and did not change for subsequent cycles (Figure 4.9A – 4.9B, top images). This trend was attributed to swelling of the charged polymer segments (PDMH) when under water. AFM phase images of the films after water submersion also exhibited features of swelling and morphological changes after the initial submersion but did not change after subsequent submersions (Figure 4.9, bottom images). This stability over subsequent submersions suggested that the surface reached an equilibrium under water after the initial submersion cycle. The PS regions appeared below the PDMH domains, which is consistent with reducing interfacial contact with water for these hydrophobic domains.
Additionally, the domain spacings ($L_0$) of the BBCP films decreased after initial water submersion and then tended to have constant $L_0$ values for subsequent submersions (Figure 4.9 and Table 4.2). He et al. demonstrated that the long alkyl chain pendant groups off the quaternary ammonium polymers which were grafted from silica oxide surfaces rearranged to inside the brush block polymer chains to avoid unfavorable interfacial energy from contacting with water. The significant reduction in $L_0$ values for a BBCP with $f_{\text{PDMH}}$ of 0.73 may result from the predominant swelling of the ammonium groups of the PDMH segment on the surface with the aggregation of six-carbon alkyl pendant groups off the quaternary ammonium groups and twelve-carbon alkyl chains of the RAFT CTA underneath the bottle brush structures. Since the morphology of BBCP films seemed to not change after the initial submersion cycle, other BBCPs films of PS$_{17}$-b-PDMH ($f_{\text{PDMH}}$ of 0.58) with DP of 100:50 and 50:25 and BBCPs films of PS$_{39}$-b-PDMH ($f_{\text{PDMH}}$ of 0.40) with DP of 100:50 were imaged only after the initial submersion cycle. The similar trends of the swelling features and morphology change were observed in the AFM phase images (Figure B.5A and B.6A).
Figure 4.9. AFM height images (top) and phase images (bottom) of films of PS\textsubscript{17}-b-PDMH before and after 3 immersion cycle under water; 1-cycle for 3 hours, 2-cycle for 6 hours, and 3 cycle for 3 days. A) PS\textsubscript{17}-b-PDMH film with $f\text{PDMH} = 0.58$ and B) PS\textsubscript{17}-b-PDMH film with $f\text{PDMH} = 0.73$.

One of the factors governing the self-organization of BBCPs was likely the solvent evaporation rate from each domain, which consequently kinetically influences the phase segregation. This approach led the BBCPs to likely not obtain equilibrium phase structures. Thermal annealing above the $T_g$ of both polymers (110 °C for 17 h) prior to AFM analysis attempted to equilibrate the films after spin coating. After annealing, AFM images revealed the different morphological features as demonstrated by larger phase separated domains on the surfaces as compared to the BBCP films as casted (Figures B.1B – B.3B). The $L_0$ values of thermal-annealed films were also significantly larger than that of casted films, suggesting that the thermal
annealing favored more self-assembly of the polymer side chains (Table 4.2). The morphology of the thermal-annealed film did not change despite longer annealing time (21 h), suggesting that 17-hour thermal annealing was long enough to equilibrate the BBCP films (Figure B.7).

Fast Fourier Transform (FFT) of AFM phase images was utilized to evaluate the extent that the morphology was ordered, since higher ordered nanostructures are expected to yield sharper contrast of the FFT circles. FFT images of annealed film showed more discrete center than that of unannealed films, suggesting that the heating allowed the BBCPs to phase separate into more stable and ordered features (Figure 4.5A – 4.5B). After 3-cycles of water submersion, the thermally annealed PS$_{17}$-b-PDMH films with DP of 200:100 ($f_{\text{PDMH}} = 0.58$) exhibited stable morphology despite the increasing surface roughness from swelling of the PDMH domains (Figure 4.5C, top images and Table 4.3). Additionally, the surface roughness of annealed films increased less after submersion than roughness of unannealed films upon submersion. These results supported that thermal annealing created more stable morphologies driven by thermodynamic phase separation. However, the $L_0$ values for BBCP films significantly increased after initial submersion and drastically decreased after sequential submersion cycle. For thermally annealed films with high $f_{\text{PDMH}}$ of 0.73 of PS$_{17}$-b-PDMH with DP of 100:100 demonstrated the swelling features accompanied with gradually roughening surfaces and changing morphology after 3 submersion cycle (Figure B.8). After initial submersion, AFM images showed the slightly swelling pattern of the PDMH domains on the surface and the spherical domains of PS showed aggregation underneath the swelling PDMH domains. After 3 submersion cycle, the spherical regions became larger and more noticeable on the surfaces whereas the $L_0$ values decreased (Figure B.8 bottom). This occurrence was likely due to more aggregation of alkyl pendant groups off PDMH polymer segments and the long alkyl chain of RAFT CTA after submerged for longer time. Likewise, such morphology change and significant reduction of the $L_0$ values was clearly observed on the BBCP.
films of PS$_{39}$-b-PDMH with DP of 50:100 ($f_{\text{PDMH}} = 0.70$) after the initial submersion process for 3 h. (Figure B.9). Interestingly, the thermal-annealed films of PS$_{39}$-b-PDMH ($f_{\text{PDMH}}$ of 0.40) with DP of 100:50 exhibited the likelihood of phase separated morphological consistency and slightly increase of the surface roughness and the $L_0$ values.

Figure 4.10. AFM phase images and inserted fast Fourier transform (FFT) images of BBCP thin films. A) AFM images and its FFT images of BBCP films of PS$_{17}$-b-PDMH with 200:100 prepared by non-annealing method (the left image) and thermal annealing method (the right image). B) AFM images and its FFT images of BBCP films of PS$_{39}$-b-PDMH with 100:50 prepared by non-annealing method (the left image) and thermal annealing method (the right image). C) AFM height images (top) and phase images (bottom) of thermal-annealed films of PS$_{17}$-b-PDMH with $f_{\text{PDMH}} = 0.58$ and DP of PS:PDMH of 200:100 before and after water submersion for 3 submersion cycle.

In addition to AFM analysis, static water contact angles were measured to evaluate the wettability of some BBCP films before and after water submersion (Figure B.10). Before water submersion, most of the unannealed BBCP films exhibited hydrophilic surfaces as demonstrated
by low water contact angle (25° - 40°), while the thermal annealed films had higher water contact angles (60° - 70°) (Figure 4.6 and Table 4.3). Nevertheless, after water submersion, the unannealed surfaces became more hydrophobic as demonstrated by contact angles above 60°. Such higher water contact angle values were likely due to high degree of film roughness after soaked under water (Table 4.3). Accordingly, the less degree of roughening surfaces of thermally annealed films showed corresponding less discrepancy of water contact angle of films before and after submersion compared to those of unannealed films.78,148

Table 4.3. Static water contact angle measurement of BBCP thin films before and after water submersion

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[NB-PS]$<em>{10}$-[NB-PDMH]$</em>{0}$</th>
<th>Water contact angle$^{a}$ (°)</th>
<th>Roughness$^{b}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unannealed films</td>
<td>Thermal-annealed films</td>
<td>Unannealed films</td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
</tr>
<tr>
<td>PS$_{25}$-b-PDMH</td>
<td>100:50</td>
<td>79±2</td>
<td>77±5</td>
</tr>
<tr>
<td>PS$_{25}$-b-PDMH</td>
<td>200:100</td>
<td>39±2</td>
<td>63±2</td>
</tr>
<tr>
<td>PS$_{25}$-b-PDMH</td>
<td>100:100</td>
<td>16±3</td>
<td>61±8</td>
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<td>100:50</td>
<td>70±1</td>
<td>79±2</td>
</tr>
<tr>
<td>PS$_{50}$-b-PDMH</td>
<td>100:100</td>
<td>40±5</td>
<td>76±3</td>
</tr>
<tr>
<td>PS$_{50}$-b-PDMH</td>
<td>50:100</td>
<td>25±9</td>
<td>75±3</td>
</tr>
</tbody>
</table>

$^{a}$Average water contact angle and standard deviation values were calculated from 6 analyzed spots of 2 replicate films, combining the angle values derived from the left and the right angles.

$^{b}$Roughness (R$_{rms}$) determined from AFM height images before and after water submersion and reported as average ± standard deviation from 3 AFM phase images.
4.4. Conclusion.

A successful procedure to create novel amphiphilic bottlebrush block copolymers with high charged density of quaternary ammonium polymers (PDMH) by a grafting-through ROMP approach. Sequential polymerization of NB-PS and NB-PDMH provided well-defined bottlebrush...
architectures with asymmetric side chain lengths of PS_{39-b}-PDMH, and the desired PDMH compositions in the molecular chains (f_{PDMH} = 0.5 and 0.75 for PS_{17-b}-PDMH, and f_{PDMH} = 0.4 - 0.7 for PS_{39-b}-PDMH). AFM images demonstrated distinct phase separation of BBCPs on thin films. The BBCP thin films exhibited morphological transitions corresponding to varied f_{PDMH} and asymmetry of polymer side chains lengths. To study the stability of phase separated morphology on thin films, the unannealed films demonstrated the morphology change with the roughening surfaces after water submersion. The alteration was likely due to the swelling of the PDMH polymer segments and aggregation of pendant six-carbon alkyl chain and the twelve-carbon alkyl chains of RAFT CTA under water. Since the non-annealing method enabled the self-assembled BBCPs not to approach the equilibrium on thin films, thermally annealing method was utilized to prepare more stable morphology. The thermally annealed films of PS_{17-b}-PDMH with f_{PDMH} of 0.5 with DP of 200:100 exhibited morphological consistency on thin films after 3 immersion cycles despite slightly roughening surfaces. Likewise, the thermally annealed film of PS_{39-b}-PDMH with f_{PDMH} of 0.4 with DP of 100:50 showed morphology stability after submersion for 3 h. On the other hand, thermal-annealed BBCP films with high f_{PDMH} could not maintain morphology stability under water. In addition to phase segregated morphology analyzed by AFM, the wettability of the BBCP surfaces, which were analyzed by water contact angle measurement, demonstrated that the BBCPs films after water submersion became more hydrophobic compared to the corresponding hydrophilic dry films by significant increase of water contact angle values. This result was likely due to the increase of surface roughness of BBCP films after water submersion. The water contact angles of thermally annealed films, which had fewer roughening surfaces after water submersion, slightly increased, suggesting that the BBCP surfaces were more hydrophobic due to the roughening surfaces. Accordingly, the BBCP coatings containing f_{PDMH} = 0.5 prepared by thermal annealing method have a potential to maintain the phase separated morphology after water.
submersion. The results suggest that such a coating can be used to further study about antifouling and antimicrobial performance. Additionally, the potential procedure could develop to generate high dense cationic bottlebrush block copolymers that can expand the usage of cationic bottlebrush based polymer coatings for other applications.
CHAPTER 5

5.1 Future work

As mentioned in chapter 3, well-defined cationic bottlebrush homopolymers of PDMAEA-C6-Br14 were successfully synthesized with the desired MW by ROMP. However, the halide ligand exchange between bromide and iodide counter anions of quaternary ammonium MMs and Grubbs catalyst slowed ROMP propagation rate due to less active substituted Grubbs catalyst than the original Grubbs catalyst (G3). Less active catalysts, bromide-substituted G3 or iodide-substituted G3 catalysts, are likely to impede the polymerization to achieve high % MM conversion of high molecular weight quaternary ammonium MMs. Additionally, the quaternary ammonium MMs containing six-carbon alkyl chains with chloride counter anions were challenging to be synthesized through quaternization reaction due to a bad leaving group of chloride ions compared to bromide and iodide ions. To improve the challenges, polymerization of quaternary ammonium MMs containing six-carbon pendent groups with different counter anions that are tolerant to chloride ligand substitution of G3 catalyst is an alternative way. It is known that functional groups such as amines, carboxylates, and hydroxyl groups could affect the activity of ruthenium complexes during metathesis reactions.118,149,150,151 Moreover, the chloride ligands of the ruthenium complex were replaced with trifluorosulfonates or trifluorocarboxylate.152 Tosylate (TsO−) group is one of the leaving groups that can be utilized to generate quaternary ammonium monomers.153 So, quaternary ammonium MMs with tosylate anions can be afforded by quaternizing tertiary amine MMs of NB-PDMAEA with hexyl p-toluenesulfonate. The tosylate anions MMs may help mitigate halide ligand exchange occurred during ROMP, consequently promoting ROMP of high MW of quaternary ammonium MMs.

As demonstrated by AFM analysis in chapter 4, the self-assembled BBCP thin films of PS17-b-PDMH with fPDMH~ 0.5 prepared by thermal annealing method are likely to maintain the phase
separated morphologies after water submersion for 3 days. So, the BBCP thin film of PS$_{17}$-b-PDMH with DP of 200:100 will be further studied for antifouling efficiency. To scrutinize the polymer surface compositions, x-ray photoelectron microscopy (XPS) can be utilized to evaluate carbon and nitrogen elements on thin films before and after water submersion.\textsuperscript{39} Prior to the study of the antimicrobial performance of the self-assembled thin films under PBS solution, the stability of the phase separated morphology of BBCP thin films will be examined by submersion of the BBCP thin films under PBS solution for 3 immersion cycle and then analyzed by AFM analysis. After that, antibacterial efficiency of BBCP thin films against bacteria (Escherichia coli) can be conducted and quantitatively analyzed by fluorescence microscopy to evaluate the alive and dead cells of bacteria on the BBCP thin films.\textsuperscript{37,38,39} The bacteria colonization on the BBCP thin films can be characterized by a scanning electron microscope (SEM).\textsuperscript{34}
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Figure A.1. $^1$H-NMR spectrum of NB-RAFT CTA
Figure A.2. $^1$H-NMR spectrum of purified PDMAEA macromonomer with 24 DP (PDMAEA$_{24}$)
Figure A.3. Figure S7. $^1$H-NMR spectrum of NB-PDMAEA-C6-I macromonomer with 14 DP (NB-PDMAEA-C6-I$_{14}$)
Figure A.4. $^1$H-NMR spectrum of NB-PDMAEA-C12-Br macromonomer with 14 DP (NB-PDMAEA-C12-Br$_{14}$)
Figure A.5. $^1$H-NMR spectrum of NB-PDMAEA-C6-Br macromonomer with 19 DP (NB-PDMAEA-C6-Br$_{19}$)
Figure A.6. $^1$H-NMR spectrum of NB-PDMAEA-C6-I macromonomer with 19 DP (NB-PDMAEA-C6-I$_{19}$)
Figure A.7. $^1$H-NMR spectrum of NB-PDMAEA-C12-Br macromonomer with 19 DP (NB-PDMAEA-C12-Br$_{19}$)
Figure A.8. $^1$H-NMR spectrum of purified quaternary ammonium PDMAEA polymer with bromide counter ions with 24 DP (PDMAEA-C6-Br$_{24}$)
Figure A.9. $^1$H-NMR spectrum of purified quaternary ammonium PDMAEA polymer with iodide counter ions with 24 DP (PDMAEA-C6-I$_{24}$).
Figure A.10. SEC traces of aliquots at different reaction time of cationic bottlebrush homopolymers synthesized via ROMP with MM:G of 50:1 in DCM with $[\text{MM}]_0 = 0.03 \text{ M}$, $[\text{G}]_0 = 5.73 \times 10^{-4} \text{ M}$. A) PDMAEA-C6-Br$_{14}$. B) PDMAEA-C6-I$_{14}$. 
Figure A.11. A). Plot of concentration of unreacted MM as a function of polymerization time of ROMP of NB-PDMAEA-C6-Br$_{14}$ with ratio of MM:G of 50:1 in DCM (Table 2, run 1) to interpolate half-life times ($t_{1/2}$) for the consumption of monomer (i.e. 1/2, 1/4, 1/8, etc.). The time ($t_{1/2}$) at half concentration of unreacted MM was calculated from the linear equations of aliquots at different reaction time. B). The obtained half-life time ($t_{1/2}$) was plotted as a function of log([M]$_0$), where $t_{1/2}$ has the units of minutes, as a function of log([M]$_0$), where [M]$_0$ has the units of mM.

Since the bottlebrush polymerization of quaternary ammonium MMs did not follow pseudo first-order kinetics, the half-life method to calculate reaction order for a reactant was used to calculate the empirical monomer reaction order for the polymerization of NB-PDMAEA-C6-Br$_{14}$ with MM:G3 of 50 (Table 2, entry 1). The half-life ($t_{1/2}$) for monomer consumption between each aliquot was obtained from a plot of unreacted MM concentration versus the polymerization time (Figure S19a) and was plotted log($t_{1/2}$) as a function of log([M]$_0$) (Figure S19b). Theoretically, the plot of log($t_{1/2}$) as a function of log([M]$_0$) should be a linear line of which the slope plus 1 should be the empirical monomer consumption order. Experimentally, the plot significantly deviated from a linear relationship, suggesting the overall catalyst activity changed during ROMP. When the data kinetic data was plotted assuming pseudo second-order kinetics (1/[MM] versus time) a linear relationship resulted (Figure S20, but the calculated [MM]$_0$ (0.02 M) did not match the actual [MM]$_0$ (0.03 M). These data suggest that the overall catalyst activity
changed due halide ligand exchange in the first minute and yielded a new catalyst system and/or propagating center that better followed second order in monomer kinetics, which could be a mixture of propagating centers that have zero, one, or two exchanged ligands.
Figure A.12. Kinetic plot of $1/[\text{MM}]$ as a function of polymerization time assuming second-order kinetics where line was a linear fit of the data of ROMP of NB-PDMAEA-C6-Br$_{14}$ with a ratio of MM:G of 50:1 in DCM (Table 2, entry 1).
Figure A.13. $\ln([M]_0/[M])$ as the function of polymerization time of PDMAEA-C6-Br$_{14}$ and PDMAEA-C6-I$_{14}$ synthesized through ROMP with MM:G of 50:1 in DCM (Table 2, entries 1 and 2, $[G]_0 = 5.73 \times 10^{-4}$ M and $[MM]_0 = 0.03$ M)
Figure A.14. $\ln([M]_0/[M])$ as a function of polymerization time for PDMAEA-C6-Br$_{14}$ in DCM with MM:G of 25:1, 50:1, 74:1, and 100:1 with a constant $[G]_0$ equal to $5.73 \times 10^{-4}$ M (Table 2, entries 3–5).
Figure A.15. $\ln([M]_0/\langle M \rangle)$ as the function of polymerization time of bottlebrush homopolymer PDMAEA-C6-Br$_{14}$ synthesized via ROMP in DCM with MM:G of 25:1 by keeping $[\text{MM}]_0$ constant at 0.03 M and $[\text{G}]_0 = 1.146 \times 10^{-3}$ M (Table 2, run 6).
Figure A.16. SEC traces of cationic bottlebrush homopolymers of PDMAEA-C6-Br14 synthesized via ROMP in DCM with varied MM:G with constant $[G]_0 = 5.73 \times 10^{-4}$ M and increase $[MM]_0$ as increase MM:G (Table 2, entries 3 – 5). A) 25:1, B) 74:1 and C) 100:1.
Figure A.17. Kinetic profile of bottlebrush polymerization of NB-PDMAEA-C6-Br\textsubscript{14} with ratio of MM:G of 25:1 in DCM ([G]\textsubscript{0} = 5.73 \times 10^{-4} M and [MM]\textsubscript{0} = 0.015 M) by mixing non-polymerizable PDMAEA-C6-Br\textsubscript{24} and PDMAEA-C6-I\textsubscript{24} MMs with the G3 solution in DCM before transfer to NB-PDMAEA-C6-Br\textsubscript{14} solution (Table 2, entries 3, 9, and 10). A) % conversion as a function of polymerization time of only PDMAEA-C6-Br\textsubscript{14} (black dots), PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-Br\textsubscript{24} (red dots), and PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-I\textsubscript{24} (blue triangles). B) ln([M]\textsubscript{0}/[M]) as the function of polymerization time of only PDMAEA-C6-Br\textsubscript{14} (black dots), PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-Br\textsubscript{24} (red dots), and PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-I\textsubscript{24} (blue triangles). Lines are linear fits of the data.
Figure A.18. SEC traces of aliquots of bottlebrush polymerization of NB-PDMAEA-C6-Br\textsubscript{14} with a ratio of MM:G of 25:1 in DCM ([G]\textsubscript{0} = 5.73 \times 10^{-4} \text{ M and [MM]}\textsubscript{0} = 0.015 \text{ M}) by mixing PDMAEA-C6-Br\textsubscript{24} and PDMAEA-C6-I\textsubscript{24} MMs with the G3 solution in DCM before transfer to the NB-PDMAEA-C6-Br\textsubscript{14} solution. A) SEC traces of PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-Br\textsubscript{24}. B) SEC traces of PDMAEA-C6-Br\textsubscript{14} with PDMAEA-C6-I\textsubscript{24}. 
Figure A.19. ln([M]_0/[M]) as the function of polymerization time of bottlebrush homopolymer PDMAEA-C6-Br_{19} synthesized via ROMP in DCM with MM:G of 50:1 at [MM]_0 = 0.03 M and [G]_0 = 5.73 \times 10^{-4} M (Table 2, entry 7).
Figure A.20. Kinetic profile of cationic bottlebrush homopolymerization of NB-PDMAEA-C6-Br$_{14}$ with ratio of MM:G of 50:1 (black dots, [MM]$_{0}$ = 0.03 M) and NB-PDMAEA-C6-Br$_{19}$ with ratio of MM:G of 35:1 (red dots, [MM]$_{0}$ = 0.02 M) with equal [G]$_{0}$ = 5.73 x 10$^{-4}$ M and [Br]-$_{0}$ = 0.40 M via ROMP. A) % conversion as a function of polymerization time. B) ln([M]$_{0}$/[M]) as a function of polymerization time.
Figure A21. $^1$H-NMR spectra of crude ROMP sample of PDMAEA-C6-Br$_{14}$-b-PS$_{17}$ with MM1:MM2:G of 25:25:1 in DCM. A) Crude ROMP of 1$^{st}$ block of PDMAEA-C6-Br$_{14}$-b-PS$_{17}$ (MM1:G of 25:1) after 60 minutes. B) Crude ROMP of 2$^{nd}$ block of PDMAEA-C6-Br$_{14}$-b-PS$_{17}$ (25:25:1) after 3 minutes. C) Crude ROMP of 2$^{nd}$ block of PDMAEA-C6-Br$_{14}$-b-PS$_{17}$ (25:25:1) after 30 minutes.
Figure A.22. $^1$H-NMR spectra of crude ROMP of PS$_{17}$-b-PDMAEA-C6-Br$_{14}$ with MM1:MM2:G of 25:25:1 in DCM. A) Crude ROMP of 1$^{st}$ block of PS$_{17}$-b-PDMAEA-C6-Br$_{14}$ (MM1:G of 25:1) after 3 minutes. B) Crude ROMP of 2$^{nd}$ block of PS$_{17}$-b-PDMAEA-C6-Br$_{14}$ (MM1:MM2:G of 25:25:1) after 60 minutes.
Table B.1. Characteristics of norbornene-functionalized macromonomers

<table>
<thead>
<tr>
<th>Macromonomer (MMs)</th>
<th>$M_{n(NMR)}$ [g mol$^{-1}$]</th>
<th>$M_{n(SEC)}$ [g mol$^{-1}$]</th>
<th>$D$ $^b$</th>
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<tbody>
<tr>
<td>NB-PS$_{17}$</td>
<td>2200</td>
<td>1700</td>
<td>1.20</td>
</tr>
<tr>
<td>NB-PS$_{39}$</td>
<td>4500</td>
<td>4000</td>
<td>1.29</td>
</tr>
<tr>
<td>NB-PDMH</td>
<td>4500</td>
<td>2600</td>
<td>1.36</td>
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</table>

$^a$Calculated from DP of MMs determined from $^3$H-NMR spectra by end group analysis (DP x MW of styrene monomer or DMAEA monomer) + MW of NB-RAFT CTA for NB-PS$_{17}$, NB-PS$_{39}$, and NB-PDMH, respectively. $^b$Obtained from SEC analysis in DMF with 0.5 wt% LiBr with linear PS standards.
Figure B.1. AFM images of unannealed films and thermally annealed films of PS$$_{17}$$-b-PDMH with $$f_{\text{PDMH}}$$ of 0.58 and varied DP of PS:PDMH. A) PS$$_{17}$$-b-PDMH films as casted and B) thermally annealed PS$$_{17}$$-b-PDMH films.
Figure B.2. AFM images of unannealed films and thermally annealed films of PS$_{17}$-b-PDMH with $f_{\text{PDMH}}$ of 0.73 and varied DP of PS:PDMH. A) PS$_{17}$-b-PDMH films as casted and B) thermally annealed PS$_{17}$-b-PDMH films.
Figure B.3. AFM images of unannealed films and thermally annealed films of PS39-b-PDMH with varied \( f_{\text{PDMH}} \) and DP of PS-PDMH. A) PS39-b-PDMH films as casted and B) thermally annealed PS39-b-PDMH films.
Figure B.4. AFM images of unannealed films and thermally annealed films of PS$_{39}$-b-PDMH with varied f$_{PDMH}$ of 0.55 and DP of 100:100 before and after initial submersion cycle for 3 h. A) PS$_{39}$-b-PDMH films as casted and B) thermally annealed PS$_{39}$-b-PDMH films.
Figure B.5. AFM images of unannealed films of PS$_{17}$-b-PDMH with varied $f_{\text{PDMH}}$ of 0.58 and varied DP of PS:PDMH before and after initial submersion cycle for 3 h. A) PS$_{17}$-b-PDMH films with DP of 100:50 and B) PS$_{17}$-b-PDMH films with DP of 50:25.
Figure B.6. AFM images of unannealed films and thermally annealed films of PS$_{39}$-b-PDMH with varied $f_{\text{PDMH}}$ of 0.40 and DP of 100:50 before and after initial submersion cycle for 3 h. A) PS$_{39}$-b-PDMH films as casted and B) thermally annealed PS$_{39}$-b-PDMH films.
Figure B.7. AFM images of thermally annealed films of PS_{17}-b-PDMH with DP of 100:100 and 100:50 after thermal annealing at 110 °C for 17 h and then 21 h.
Figure B.8. AFM height images (top) and phase images (bottom) of the thermally annealed films of PS$_{17}$-b-PDMH with $f_{\text{PDMH}}$ of 0.73 and DP of 100:100 before and after 3 submersion cycle under water; 1-cycle for 3 hours, 2-cycle for 6 hours, and 3 cycle for 3 days.
Figure B.9. AFM height images (top) and phase images (bottom) of the thermally annealed films of PS_{39}-b-PDMH with $f_{\text{PDMH}}$ of 0.70 and DP of 50:100 before and after initial submersion cycle under water for 3 h.

Roughness (nm) 3.7 ± 0.1
$L_0$ (nm) 141 ± 2

Roughness (nm) 6.3 ± 0.5
$L_0$ (nm) 128 ± 2
Figure B.10. Representative water contact angle images of unannealed films and thermal-annealed films of PS$_{17}$-b-PDMH with $f_{\text{PDMH}} = 0.58$ and DP of PS:PDMH as 200:100 before and after water submersion for 3 h.
Figure B.11. AFM images and cross-sections of height images of the unannealed film of PS$_{39}$-b-PDMH with DP of 50:100 at different 3 positions (the arrows identified the measured positions). The cross-sectional lines were fitted a plane through three points. The polymer thicknesses were averaged to provide 173 ± 15 nm (the error was a standard deviation).
APPENDIX B.12. CALCULATION OF VOLUME FRACTION OF PDMH ($f_{\text{PDMH}}$) IN A BOTTLEBRUSH BLOCK COPOLYMERS.

Volume fraction of PDMH was determined from ratios of volume of PDMH to total volume of PDMH and PS as provided in equation 1, by using density of PDMH (0.915 g/mL) and PS (1.04 g/mL).

$$f_{\text{PDMH}} = \frac{V_{\text{PDMH}}}{V_{\text{PDMH}} + V_{\text{PS}}} \quad \text{(Equation B.12)}$$

An example of volume fraction calculation of PS$_{17}$-b-PDMH with initial ratios of [NB-PS]$_0$:[NB-PDMH]$_0$:[G3]$_0$ of 100:50:1, sequential ROMP achieved 100% NB-PS$_{17}$ conversion for the PS macroinitiator polymerization and 97% NB-PDMH conversion to yield the resulting BBCP with DP of PS:PDMH of 100:48.5.

- Calculation of volume of PDMH ($V_{\text{PDMH}}$) per a mole of BBCP

$$\frac{48.5 \text{ mol of NB-PDMH}}{1 \text{ mol of BBCP}} \times \frac{14 \text{ RU of PDMH}}{1 \text{ mol of NB-PDMH}} \times \frac{308.18 \text{ g of PDMH}}{1 \text{ RU of PDMH}} \times \frac{1 \text{ mL of PDMH}}{0.915 \text{ g of PDMH}} = \frac{228,693.2 \text{ mL of PDMH}}{1 \text{ mol of BBCP}}$$

- Calculation of volume of PS ($V_{\text{PS}}$) per a mole of BBCP

$$\frac{100 \text{ mol of NB-PS}}{1 \text{ mol of BBCP}} \times \frac{17 \text{ RU of PS}}{1 \text{ mol of NB-PS}} \times \frac{104.15 \text{ g of PS}}{1 \text{ RU of PS}} \times \frac{1 \text{ mL of PS}}{1.04 \text{ g of PS}} = \frac{170,245.2 \text{ mL of PS}}{1 \text{ mol of BBCP}}$$

- Calculation volume fraction ($f_{\text{PDMH}}$) from equation 1

$$f_{\text{PDMH}} = \frac{228,693.2 \text{ mL of PDMH}}{228,693.2 \text{ mL of PDMH} + 170,245.2 \text{ mL of PS}} = \frac{228,693.2 \text{ mL of PDMH}}{398,938.4 \text{ mL of total}} = 0.58$$

$$f_{\text{PS}} = 1 - f_{\text{PDMH}} = 1 - 0.58 = 0.42$$
Volume fraction calculation of other BBCPs was determined with the provided method by using the DP of PS:PDMH calculated from % MM conversion and initial ratios of [NB-PS]₀:[NB-PDMH]₀:[G3]₀ (Table 3.2).
BIOGRAPHY OF THE AUTHOR

Hathaithep Senkum was born on May 16th, 1988 in Bangkok, Thailand. She was raised and lived until she graduated from High school. Hathaithep pursued her a bachelor’s degree in Chemistry at Chulalongkorn University, Bangkok, Thailand. After graduation in 2010, she worked for petroleum and lubricant company in Thailand for 2 years. Her goal was to earn doctorate degree in polymer chemistry in the united states. In 2014, she moved to Chicago to study English language in a program named English as a second language (ESL) for year before she attended the University of Maine in August 2015 to pursue a doctorate degree in Chemistry department. She joined Dr. William M. Gramlich group which focuses on research of polymer chemistry. She has obtained the experiences of polymer synthesis, polymer characterization, and polymer surface characterization. Hathaithep is a candidate for the Doctor of Philosophy degree in Chemistry from the University of Maine in May 2021.