

Chapter 1

INTRODUCTION

BRUSH POLYMERS

Assemblies of polymer chains that are bound by one end to planar or spherical surfaces, or bound to linear polymer chains, are referred to as polymer brushes.¹ When the polymer side chains are bound to a linear polymer the steric crowding of the side chains forces the polymer backbone to be more extended, resulting in a cylindrical worm-like structure^{1,2} that can reach lengths up to a few hundred nanometers.³⁻⁶ These polymers also show little evidence of any entanglement even at ultra-high molecular weights. The structural characteristics of brush polymers has led to increased interest in their utilization for applications such as drug delivery,^{7,8} templates for inorganic particles,⁹⁻¹¹ molecular actuators,¹² and as precursors for various carbon nanostructures.^{13,14}

There are three general methods of synthesizing brush polymers: the “grafting from”, the “grafting onto”, and the “grafting through”, or the macromonomer (MM) approach (**Figure 1-1**).¹⁵ In the “grafting from” method, the side chains are polymerized from initiators sites on the polymeric backbone.¹⁶⁻¹⁸ This method provides good control of main chain polydispersity (PDI), but gives only intermediate control over the side chain PDI and the grafting density due to the high density of initiation sites on the backbone.¹⁹⁻²¹ In the “grafting onto” method, the polymer side chains are coupled onto the polymer backbone.^{15,22-24} This method allows for good main chain PDI and side chain PDI, but lacks control over the grafting density due to growing steric difficulties for the side chains to access and couple to the backbone as the conversion increases.^{19,25} In the “grafting through” or MM approach, the side chains are synthesized with a polymerizable end group, which is then polymerized to make the brush polymer.^{26,27} This method provides good side chain PDI and guarantees complete grafting of the polymer. However, some polymerization methods lack good control over the main chain length and PDI with this approach.¹⁹ Recent studies have shown that ruthenium catalyzed ring-opening metathesis polymerization (ROMP) of norbornene end functionalized MMs can help overcome the limitations of the MM approach, and has been used to yield brush polymers with excellent PDI values (<1.10) while reaching ultra-high molecular weights (MWs) (up to 1880×10^3 g/mol).^{3,28}

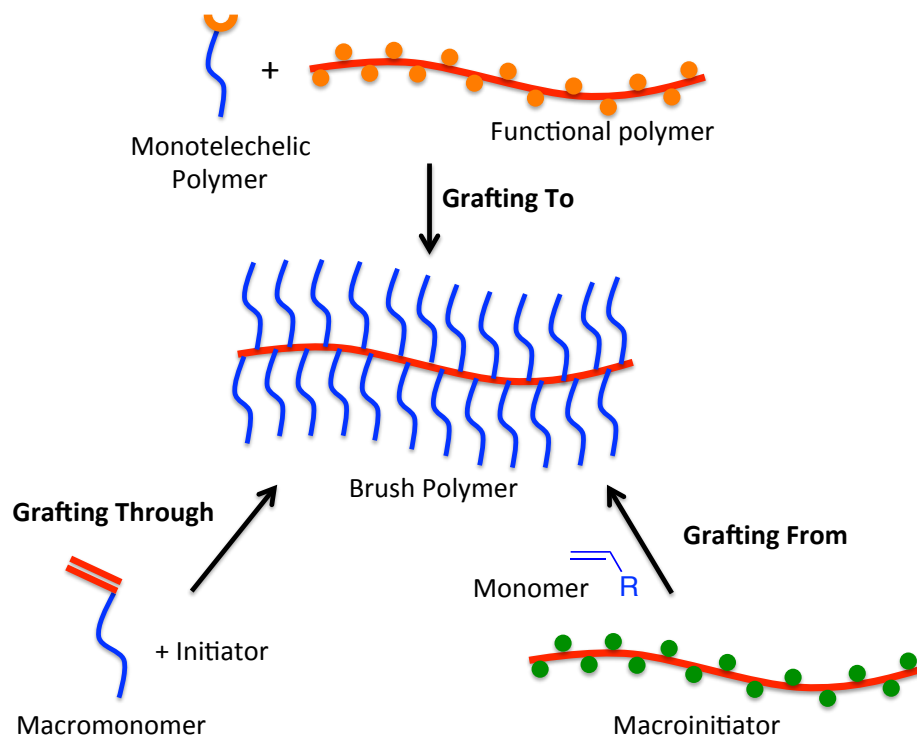
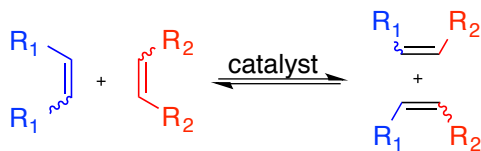


Figure 1-1. Schematic illustration of the three pathways to synthesizing brush polymers.

OLEFIN METATHESIS

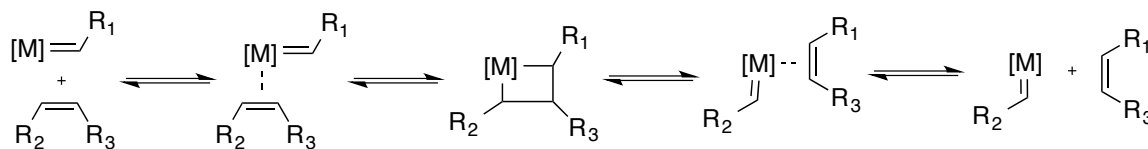
Olefin metathesis is an extremely versatile and well-reviewed reaction where a carbon-carbon double bond undergoes scission and rearrangement (**Scheme 1-1**).²⁹ The development of efficient catalysts has led to the widespread use of this reaction for applications such as insect pheromones, waxes, plasticizers, and baseball bats.^{30,31}



Scheme 1-1. A general scheme for olefin metathesis.

The mechanism of olefin metathesis starts with an olefin coordinating to the metal carbene complex, followed by a [2+2] cycloaddition with the metal carbene double bond to yield a metallacyclobutane. Next, a cycloreversion takes place, where cleavage of the newly formed bonds results

in the starting material, but the cleavage of the other two bonds in the metallocyclobutane yields a new olefin coordinated to a new metal carbene. The newly formed olefin can then dissociate from the metal center to give the desired product and a new metal carbene that can re-enter the catalytic cycle (**Scheme 1-2**).



Scheme 1-2. A general scheme for the mechanism of olefin metathesis.

Depending on the chemical structure of the desired product, several types of olefin metathesis reactions are possible. When building small molecules, the main types of metathesis used are cross metathesis (CM), ring-closing metathesis (RCM), and ring-opening cross metathesis (ROCM) (**Figure 1-2**). In cross metathesis, two terminal alkenes undergo transalkylation to yield the desired product and ethylene. Ring-closing metathesis involves an α,ω -diolefin that closes to form a ring, usually releasing ethylene in the process. Ring-opening cross metathesis involves a cyclic olefin that reacts with a linear olefin to open up the ring.

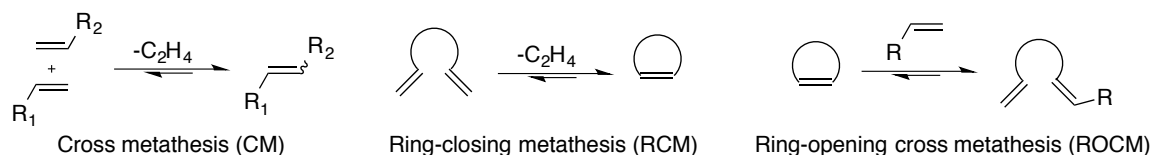


Figure 1-2. General reaction schemes for cross metathesis (left), ring-closing metathesis (center), and ring-opening cross metathesis (right).

Olefin metathesis has also proven effective in synthesizing polymers via either acyclic diene metathesis polymerization (ADMET) or the previously mentioned ROMP (**Figure 1-3**). In ADMET a diene undergoes repeated cross metathesis to give the polymer in a step polymerization. ADMET reactions are generally run under conditions of high concentration and often involve the active removal of ethylene. ROMP, on the other hand, is a chain polymerization, where the catalyst acts as an initiator for the polymerization. It is similar to ROCM, where a cyclic olefin is opened, but instead of reacting with a linear alkene to release the molecule from the catalyst, the newly opened ring reacts with another cyclic olefin to grow a polymer chain.

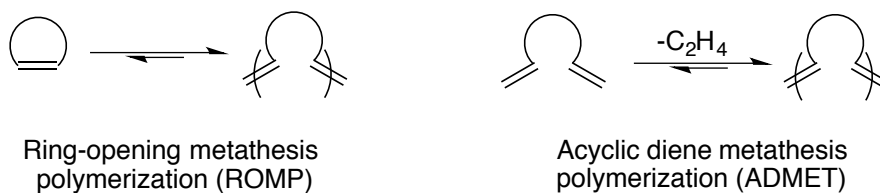


Figure 1-3. General reaction schemes for ring-opening metathesis polymerization (left) and acyclic diene metathesis polymerization (right).

In order to obtain well defined, narrowly dispersed polymers with high molecular weights via ROMP, it is important that the catalyst used exhibits both fast initiation and high reactivity. Since MMs are challenging monomers, this has been especially important when attempting to synthesize brush polymers via ROMP. Recently, it was found that the bis-pyridine derivative of the second generation Grubbs catalyst³² (**Figure 1-4**) shows fast initiation, high reactivity, and high functional group tolerance, even in the ROMP of MMs, making it a pivotal tool to advance our studies of brush polymers and their self-assembly.^{3,28,33}

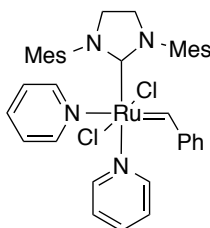


Figure 1-4. The chemical structure of the bis-pyridine derivative of the second-generation Grubbs catalyst.

BRUSH COPOLYMER SELF-ASSEMBLY

Utilizing the highly reactive and fast-initiating bis-pyridine derivative of the second-generation Grubbs catalyst, Xia *et al.* started exploring the self-assembly of both random and block brush copolymers (**Figure 1-5**) using small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM).³ The brush copolymers used were synthesized from poly lactide (PLA) and poly (*n*-butyl acrylate) (PnBA) based MMs.

The brush random copolymers showed close to identical domain spacing (as measured by SAXS) regardless of the degree of polymerization (DP) of the backbone, suggesting a microphase

segregation of the side chains, with the poly norbornene backbone localized at the interface between the PLA and PnBA domains (**Figure 1-6 top**).³

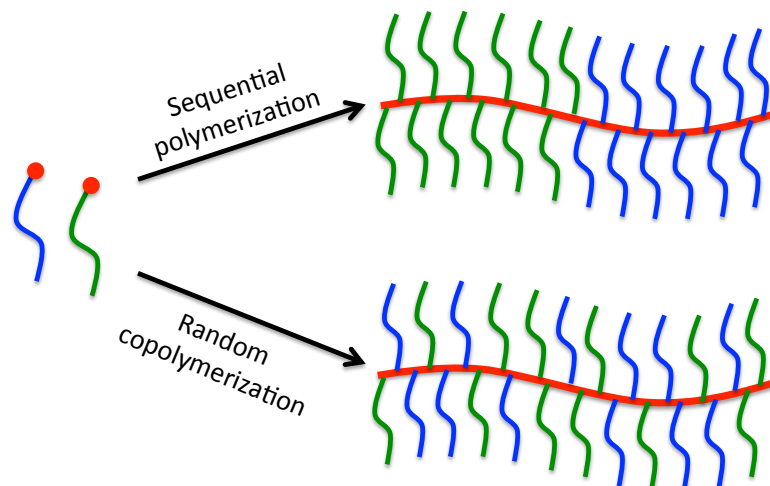


Figure 1-5. Schematic illustration of a block brush copolymer (top) and a brush random copolymer (bottom) synthesized from MMs.

The brush block copolymers (BCPs), on the other hand, showed the domain spacing to be dependent on the backbone length. The observed length was close to the expected length given a fully extended backbone. It was inferred from these results that the brush BCPs gave interdigitated packing of the polymers in a lamellar structure (**Figure 1-6 bottom**). Furthermore, Xia *et al.* found that these brush BCPs could reach domain spacing large enough to reflect visible light.³

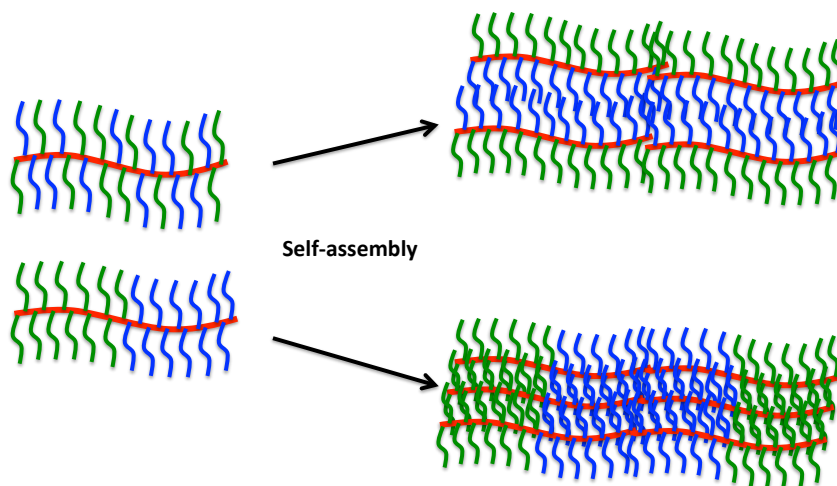


Figure 1-6. Proposed self-assembly of a brush random copolymer (top) and a brush block copolymer (bottom).

This thesis describes further studies on the self-assembly of brush polymers. *Chapter 2* discusses the self-assembly of brush BCPs into tunable photonic crystals that reflect light from the ultraviolet (UV) region and into the near infrared (NIR) region.³⁴ *Chapter 3* reports on studies on the self-assembly of symmetrical brush BCPs in bulk and thin films.^{35,36} These studies were done in collaboration with the Russell group at University of Massachusetts - Amherst, where we synthesized all the materials and they conducted the SAXS measurements and the imaging of the self-assembled samples. *Chapter 4* describes initial investigations on the self-assembly of asymmetrical brush BCPs. Finally, *Chapter 5* discusses studies on the capability of macromolecules to interdigitate into densely grafted brush copolymers using stereocomplexation as a driving force for the macromolecule/brush copolymer interactions.³⁷

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