USE OF CHAIN GROWTH POLYCONDENSATION VIA SUBSTITUENT EFFECTS FOR
THE DEVELOPMENT OF NEW POLYMER BRUSH SYSTEMS

by

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ABSTRACT

Polymers are extensively used as the main component of many coating technologies. Attachment strategies to produce polymer films with advanced functionalities have evolved from a top down technique to embody more of a bottom up approach, where thin films are actually grown from the substrate of interest. This grafting from technique has allowed for the development of polymer films with advanced architectures and improved functionality through the use of controlled/living radical polymerization (LRP) techniques that produce random coil polymers. These polymers, however, are unable to exhibit properties that polymers with more rigid character possess. The ability to produce brush films with polymers that are more elongated and have the ability to order with one another in a more of a crystalline arrangement offers the opportunity to create polymer brush films with impressive new performance properties.

In order to prepare brushes from rigid polymers, it is imperative to employ a chain growth condensation (CGC) polymerization technique in place of the more conventional step growth method. The two procedures employed to achieve CGC are the activation/deactivation method through the use of substituent effects and the catalyst transfer technique used in cross coupling reactions. To date, only conjugated polymer brushes employing catalyst transfer reactions have been produced. There remains a wide variety of high performance polymers that have yet to be used in polymer brushes that can be made via the CGC process. One particular type of condensation polymer, poly(aromatic amides) or aramids, has the potential to expand the role of polymer brushes into new and exciting areas. The main goal of this dissertation is to achieve the first examples of aramid brushes using substituent effect CGC. To this effect, the synthesis of well-defined, surface-initiated poly(N-octyl-p-benzamide) brushes was demonstrated using a novel grafting from surface initiated CGC technique. Issues with the thickness and solubility of these brushes sparked interest to further understand the factors that influence the preparation of poly(benzamides) using substituent effect CGC. Studies were conducted to investigate the role
of the monomer ester substituents and initiator structure in the CGC polymerization. It was found that the monomer ester substituents play a major role in maintaining control over the polymerization, determine the overall reaction kinetics, and improving solubility of the reaction system. Experimental results and computational studies demonstrate that the overall effect of the monomer ester substituent is more dependent on the stability of the leaving group than the electrophilicity of the reacting carbonyl.

Improvements upon the preliminary aramid brushes were realized by using the expanded understanding of the CGC technique through the use of substituent effects and has allowed for the creation of thicker brushes in a shorter time period. While, this thesis work documents the synthesis of the first aramid polymer brushes and provides a more comprehensive understanding of the substituent effect CGC process, there remains a great amount of work to further understand the structure and properties of the demonstrated brushes, in addition to expanding the work to new monomer structures.
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DEDICATION

*It is my pleasure to dedicate this thesis to my grandfather, Harrison F. Edwards, whom I have never met. I believe your spirit and love for science and technology has taken root in me and my accomplishments. This thesis is a testament to what you have provided me.*
CHAPTER 1
INTRODUCTION

Since their inception, polymeric films have been at the forefront of coating technologies. Until recently, these films were primarily produced when premade polymers are applied to surfaces via a top down spray-on or dip-coating approach. Issues with these techniques include solvolytic instabilities, poor control over morphology, and the inability to produce advanced architectures has led researchers to develop more novel polymeric attachment schemes. Certain techniques, where polymers are covalently attached to surfaces using either a grafting to or grafting from technique to produce a polymer brush structure have gained significant interest, due to the inherent flexibility of these techniques and the potential applications for the resulting materials. The advent of polymer brushes has allowed researchers to create polymer films that exhibit more interesting properties, such as improved solvolytic stability, more diverse functionality, and stimuli-responsive character.\textsuperscript{1-3} The relatively new and growing area of polymer brushes has led to potential application of these systems in areas as diverse as biomaterials, catalytic systems, electronics, and sensors.

The development and growth of polymer brushes is strongly tied to the advancement of living polymerization techniques. Utilization of controlled chain growth processes, such as the various living radical polymerization (LRP) systems, has allowed for the preparation of well-defined polymer brush films with greater functionality and a wide range of architectures. It has been extensively demonstrated that the use of controlled, living chain growth process is required to have control over the thickness of the polymer brush, produce uniform film thicknesses, and to prepare brushes with more complex architectures, such as block copolymers. The vast majority of polymer brush literature over the past 15 years has focused on the use of LRP techniques, such as reversible addition-fragmentation chain transfer (RAFT) polymerization, atom transfer radical polymerization (ATRP), and nitroxide mediated polymerization (NMP).\textsuperscript{3} While these
techniques have proved to be very successful with preparing a wide range of polymer brush systems, they are primarily limited to the use of vinyl-based monomers that tend to produce random coil structures, as a result of the flexible backbones. As such, there remains a wide variety of polymer systems, such as conjugated polymers, aramids, polyethers, polyesters polybenzoxazoles, and polysulfides that have not yet been fully utilized for the formation of brushes. Arguably, the predominant factor that has limited the use of these polymers for the preparation of brushes is that they are typically not synthesized via a well-defined chain growth process.

The polymers mentioned above are typically produced using a step-growth process, where monomers randomly react with one another to slowly achieve high molecular weights at high conversion. Recently, there has been an increasing focus on methods to produce polymers traditionally prepared using the step growth technique via a well-defined chain growth process and this research has led to the development of the so called chain growth condensation (CGC) techniques. The main premise behind converting step growth to chain growth involves encouraging the monomer to react with the end group of a growing chain, instead of reacting with another monomer. The two main techniques used to achieve CGC for these polymers are the use of substituent effects for activation/deactivation and the catalyst transfer method. The first method utilizes substituent effects to effectively deactivate the monomer towards reaction with itself, while activating the end of the polymer chain, so reactions preferentially occur at the end of the polymer. The second method involves catalyst transfer and is typically employed for the production of conjugated polymers. The chain growth process occurs through a catalyst “walk,” where the catalyst moves to the end of the polymer and reinserts itself, making the end of the polymer reactive, instead of reductively eliminating, where it would be later used in a step growth manner. To date, the only examples of using CGC for brushes has been demonstrated for the production of conjugated polymers using the catalyst transfer method.
Overall, this thesis focusses on broadening the understanding of polymer brushes by producing brushes from polymers never before envisioned, specifically poly(aromatic amides) or aramids, utilizing new surface-initiated polymerization techniques. Specifically, the hypothesis of this research is that CGC via substituent effects can be used for the preparation of new aramid brushes with more rigid, aromatic backbones. Through the process of developing this new technique for the synthesis of polymer brushes, it was discovered that the underlying theories supporting CGC via substituent effects were not complete and lacked detail. As such, a fundamental study was performed to help expand the understanding of CGC via substituent effects mechanism, with the ultimate goal to apply this new knowledge to produce thicker and more controlled aramid brushes.

An extensive background, covering the scientific concepts relevant to this thesis, is presented in Chapter 2. Polymeric coatings are presented in more detail, discussing their application and methods utilized by industry for their preparation. This chapter continues by reviewing the concept of polymer brushes and why they are desired for such a wide variety of applications, with a main focus on the preparation of brushes, via the grafting from technique, using various LRP techniques. The structure that is obtained from polymers created from vinyl polymers typically contains a flexible backbone, due to the sp³ bonded carbon atoms and the polymer adopts a random coil structure. When these polymers are surface bound in a brush state, the structure of the underlying polymer remains as a random coil, but can be compressed and elongated when the spacing between the chains is reduced. Even though brushes formed using LRP techniques have been demonstrated to be useful for a wide range of applications, including stimuli responsive and protective coatings, they are significantly different than polymers that exhibit more rigid character. The semi-flexible or rigid backbones of some polymers would be interesting additions to the brush community, due to the wider variety of properties and applications they would have the opportunity to contribute.
The background continues by exploring the concept of rigid rod polymer brushes and how their experimental realization has been limited due to the difficulty with preparing polymers typically synthesized via a step growth process in a chain growth manner. The contrast between step growth and chain growth polymers is then presented, along with the literature examples of why the step growth process is not able to form well-defined polymer brushes. Following this, an introduction to the CGC process is presented by discussing the two main CGC techniques—catalyst transfer and substituent effects. This discussion will demonstrate the importance of adopting the CGC process when attempting to produce conventional step-growth polymers with well-defined molecular weights, narrow molecular weight distributions, advanced functionalities, and complex architectures. The inherent rigid rod backbones of aromatic CGC polymers and the control the process provides have an exciting place in the new and exciting field of rigid rod polymer brushes and in broadening the polymer brush field as a whole. The background concludes with the current state of this field by summarizing the relatively few examples of rigid rod polymer brushes in the literature that consists primarily of conjugated polythiophene systems.

As the background demonstrates, the field of CGC brushes is in its infancy. In fact, the only polymer brushes prepared to date using this technique are based on conjugated aromatic polymers using surface bound initiators designed for the chain growth Kumada coupling process. While this work is exciting and demonstrates the potential oriented conjugated polymers has in future organoelectronic devices, there are a wide variety of polymers and applications that have still not been addressed, such as polymers that exhibit impressive mechanical, thermal, and chemical stability. In response to this, Chapter 3 demonstrates the first example of the preparation of aramid brushes using CGC via substituent effects and was published in Macromolecules. This exciting work was realized by first developing a new CGC initiator that consists of two functionalities. The first functionality was developed to allow the initiator to be attached to silica surfaces via the extensively studied silane chemistry. The second functionality, located para to
the attachment functionality, is the activated reactive site of the initiator, which is composed of an ester and allows for the addition of monomer in a chain growth manner, producing a brush emanating from the surface.

To demonstrate the usefulness of this surface initiator, a solution version, with an inert dimethylamide functionality, was prepared and proven to produce living and controlled polymers using CGC via substituent effects using the monomer methyl 4-(octylamino)benzoate. Next, the successful deposition of the silane CGC initiator on silicon wafers and silica nanoparticles was demonstrated using grazing angle attenuated total reflectance Fourier transform infrared (GATR-FTIR) spectroscopy, ellipsometry, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Polymer brushes were then grown from the surface by exposing the surface initiator modified substrates to deprotonated monomer solutions. The resulting polymer brushes were extensively characterized by degrafting from the nanoparticles using aqueous HF and studied using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). The synthesis procedure was proven to be reproducible, controllable, and followed the same process as a similar polymerization in solution by comparing results to the solution polymerization kinetics. Even though the development and preparation of aramid polymer brushes was an exciting new contribution to the literature and the first example of the preparation of aramid brushes using any polymerization technique, the results indicated that there were a few difficulties inherent to the specific system that was employed, which limited the thickness of the produced polymer brush films.

The results from Chapter 3 demonstrated that the produced polymer brush films had a limiting thickness. It was suspected that the limited thickness was a direct result of an insoluble film that formed on the surface of the brush during the polymerization. It was also observed in the kinetic studies that in solution polymerizations the methyl ester monomer methyl 4-(octylamino)benzoate was relatively slow compared to monomers with the phenyl ester substituent in literature. In an
effort to understand the underlying processes that produced these observations, and in the pursuit of improved polymer brushes, the polymerization mechanism of CGC via substituent effects was investigated in more detail.

Chapter 4 contains the work, submitted for publication, on how the nature of the ester substituent of the monomer affects the solubility of the polymer and other by-products of the polymerization, along with the kinetics of the CGC of the different monomers. This study involved the synthesis of different monomers with ester substituents ranging from straight or branched alkyl chains to para substituted phenyl rings. The resultant monomers were polymerized using CGC with a reactive phenyl ester initiator and it was observed during these polymerizations that the different monomers produced reaction solutions that varied in both solubility and kinetics. In an attempt to explain these results, the published mechanism for CGC via substituent effect was examined. From this, it was determined that the literature emphasis on the electrophilicity of the reacting ester carbonyl carbon on the polymer end group was not sufficient to explain the results obtained in this study. This issue was resolved by both examining earlier literature investigating the reactivity of small molecule benzoate esters towards aminolysis and by using computational modeling, conducted by the Vyas group at Colorado School of Mines. The expanded analysis of the results in this chapter demonstrated that the polymerization control, by-product solubility, and reaction kinetics depend more on the stability of the leaving alkoxide or phenoxide group than the electrophilicity of the reacting ester carbonyl carbon. These findings provide, for the first time, an expanded view of the mechanism for CGC via substituent effects and contributes to an increased understanding over to how obtain improved control in this reaction.

The more reactive nature of certain monomers in the previous study introduced some difficulties in controlling the polymerization and Chapter 5 is used to investigate how control over the polymerization can be achieved through the use of various initiators, as well as, examining the process of self-initiation. This chapter begins by studying the self-initiation for the two more
reactive phenyl ester monomers (phenyl and trifluoromethyl phenyl) with the methyl ester monomer as a control. These experiments were conducted by running polymerization reactions with no initiator and either one equivalent or 10 equivalents of the milder lithium hexamethyldisilazide (LiHMDS) base. Results from these studies demonstrated that polymer forms without the use of initiators and the overall polymerization rate occurs at a relatively swift pace with one equivalent of base and much slower using 10 equivalents. The strength of the non-nucleophilic base and the nucleophilicity of the base is also addressed by demonstrating that controlled polymers can be produced from a previously reported unsuccessful polymerization using lithium diisopropylamide base in literature. The role of initiator structure was also investigated to see how substituent effects influence the initiation effectiveness. Results from this study suggest that initiators activated through incorporation of electron withdrawing substituents improve the initiation effectiveness, by producing polymers with well-defined molecular weights and narrow molecular weight distributions. These results allow for a more complete understanding of the processes that occur during the polymerization of more reactive monomers, by addressing the potential for self-initiation and the important roles that initiators play with controlling the reaction.

The work presented in Chapters 4 and 5 contributed to a better understanding of the CGC via substituent effects mechanism and allowed for an advancement in the preparation of chain growth aramids. The results obtained from these studies also allowed for improvements upon the polymer brush system originally employed in Chapter 3 and Chapter 6 presents the very exciting preliminary results achieved when employing the lessons learned in the previous chapters. The CGC brush polymerization in Chapter 3 was improved by replacing the methyl ester monomer system with a more reactive phenyl ester initiator and monomer systems that release the more soluble lithium phenoxide by-products and polymerize at a faster rate, to produce a thicker polymer brush system in a shorter amount of time. Aramid brushes were successfully grown from
silicon wafers and visible films were measured to be 5 times thicker than the methyl brushes produced in Chapter 3, with thicknesses approaching 50 nm. High surface area studies on silica nanoparticles demonstrated that very smooth core-shell structures were apparent on the silica nanoparticles using transmission electron microscopy. The improvements obtained from the results of this study opens the door for research to be expanded and encompass the potential to use functional monomers to produce more advanced aramid brush architectures.

The thesis concludes with a consolidated summary and a list of important conclusions presented in Chapter 7. The insight gained from the four experimental chapters of this thesis were very important pieces necessary for the development of future aramid architectures that will lead to coatings with improved functionality and properties. An outline of potential directions that this research could be taken will be presented as well, specifically by introducing interesting architectures that were envisioned at the beginning of this project, but could not be realized, due to the issues that surrounded the preliminary work.
2.1 Surface Coatings

Surfaces of materials continue to be an exciting area of materials science research due to the wide variety of properties and functions they provide. Surfaces are the areas of materials where the bulk interacts with the surrounding environment. Structure-property relationships are the forefront of understanding the behavior of materials and this notion also applies to surfaces. The issue with surfaces, however, is that the chemical structure/morphology is typically not well defined, and, therefore, surfaces have the opportunity to exhibit properties different than the bulk material. It is important to be able to tailor the surface structure and properties to serve a desired purpose. One way to achieve a particular role for surfaces is to chemically modify the surface or apply a material coating. According to the Encyclopedia Britannica, surface coatings are identified as “any mixture of film-forming materials plus pigments, solvents and other additives, which applied to a surface and cured or dried yields a thin film that is functional and often decorative.” While this definition is relatively broad, conventional surface coatings are typically composed of organic films that are placed on a variety of different substrates. The result usually produces a more versatile composite material that retains the underlying bulk properties and has a modified surface that serves a desired purpose, such as protecting the underlying material.

2.1.1 Importance & Significance of Surface Coatings

Surface coatings are employed when a surface of a particular material is unable to serve a desired purpose. Typically, coatings are used to improve the surface by extending the life of the underlying material and improving the resistance to wear or chemical attack. Due to the multifunctional services that coatings can provide, there are many applications that benefit from their use with some examples including adhesives, composite/multi-function coatings, biomedical, membranes, and protective coatings. Coating technologies span many
disciplines and serve many purposes. The incredible amount of applications that incorporate coating technologies all rely on the same premise that modification of the surface properties by either chemical modification or applying a film allow for a desired surface property previously not allowed by the bulk material. General properties that can be modified by the utilization of coating technologies include anti-fouling,\textsuperscript{14} optical,\textsuperscript{22, 23} UV-absorbing,\textsuperscript{24} catalytic,\textsuperscript{25} and magnetic.\textsuperscript{26, 27}

One everyday example of how coatings can drastically change the surface properties of ordinary materials is changing the hydrophilicity of cotton by applying a very hydrophobic coating to the surface of the cotton fibers, see Figure 2.1.\textsuperscript{28} In this figure, the untreated cotton fabric material readily absorbs water, due to its hydrophilic surface character. In this particular example, when the cotton is treated with a thin coating of silica nanoparticles, the hydrophobicity of the surface dramatically increases, causing the water to not absorb, but bead up and roll around on the surface of the porous material instead.

![Figure 2.1. An example of how coatings can change the surface properties of even a porous cotton material, where an applied hydrophobic coating repels water, while the untreated, hydrophilic cotton absorbs water.\textsuperscript{28}](image)

There are many processes utilized to produce the wide variety of surface coatings. Vapor deposition processes such as chemical vapor deposition (CVD)\textsuperscript{29, 30} and physical vapor deposition (PVD)\textsuperscript{31, 32} can be used to apply thin films to surfaces. Chemical modifications such as metal...
conversion coatings\textsuperscript{33} and electrochemical plating\textsuperscript{34} can also be used to modify the surfaces to produce corrosion resistant coatings. The more familiar coating technologies involve modifying surfaces with organic materials and involve many different process, including spray coatings,\textsuperscript{35} roll to roll processing,\textsuperscript{36} along with spin and dip coatings.\textsuperscript{37}

2.2 Polymer Coatings

The most common organic coating technologies employed today typically involve the application of polymers. Polymers are long chain molecules that exhibit desirable mechanical properties, the ability to adhere to surfaces, and chemical resistance when compared to their organic small molecular weight counterparts such as waxes, oils and gels.\textsuperscript{7} Two very general methods used to produce polymer coatings vary from a top down approach to a more novel bottom up approach, where the polymers are actually grown from the surface like grass grows from the ground.

2.2.1 Polymeric Film Preparation and Applications

Polymeric coatings are typically produced when a polymer of interest is applied to a surface either from a melt or solution to produce a film coating the surface. This relatively simple process, is achieved by placing polymers on substrates by dip coating, spin coating, or through solution spray methods and these techniques are typically used to produce the vast majority of polymer films used today. In general, most applications including paints, use this top down approach to apply polymers to surfaces. These surface-applied films acquire their mechanical properties and chemical stability through the use of crosslinking, but in turn, lose the potential for advanced functionality, such as stimuli responsive behavior for example.

One attachment strategy employs the favorable interactions between polymer functional groups and surfaces through attractive forces and these films are considered to be physisorbed films, due to the non-covalent interactions between the film and the substrate. More specifically,
physisorbed films typically employ block copolymers containing one block that would interact with the surface and the other block would serve the desired purpose of the polymer film. One example of physisorption is demonstrated with the block copolymer of polystyrene-block-poly(ethylene oxide). Figure 2.2 depicts the physical adsorption attachment strategy, where the more polar component of the copolymer, poly(ethylene oxide), interacts with the polar and hydrophilic quartz substrate through dipole attractive forces to adsorb the copolymer to the surface. The more inert polystyrene block then emanates from the surface to yield a physisorbed polystyrene film. Some other examples of studied physisorbed films are polypeptides self-assembling on solid surfaces, and block copolymers interacting with surfaces through microphase separation of binary polymer blends.

![Figure 2.2. A cartoon depiction of physisorption using a block copolymer of polystyrene (PS) and poly(ethylene oxide) (PEO), where the PEO physisorbs to a quartz substrate, while the polystyrene extents away from the surface in a toluene environment.](image)

The advantages to these films is that they are easy to prepare. The disadvantages with these films including low grafting densities, difficulties with copolymer synthesis, along with thermal and
solvolytical instabilities outweigh the advantages, however.\textsuperscript{1-3, 37, 42, 43} Physisorbed polymer films, like other films with non-covalent interaction forces with surfaces, have the tendency to peel off, dissolve away, or crack due to the poor interaction and structure that is obtained using this technique and have limited advanced applications due to these issues. Based on the limitations of physisorbed polymer films, research on polymer attachment quickly shifted to understand how polymer films could be covalently attached to surfaces.

### 2.2.2 Chemical Attachment of Organic Molecules to Inorganic Surfaces

An improvement upon physisorption was conceived when polymeric materials could be covalently attached to surfaces. Covalent attachment overcomes the issues that reside with physisorption by chemically linking the polymer film to the surface, which allows for a more robust attachment. One way to attach polymers to surfaces is through the use of a small molecule linker. The two most common techniques to produce uniform small molecule films are the Langmuir-Blodgett process and formation of self-assembled monolayers (SAMs).\textsuperscript{44, 45} Langmuir Blodgett films are a unique method to produce very uniform films by using amphiphilic molecules that arrange with a high degree of order at the interface of liquids. The assembled monolayers of molecules are used to create very precise films with tunable thicknesses and are applied to surfaces by immersing a substrate into a liquid through the interface that contains the self-assembled molecules. When immersed, the assembled molecular layers attach to the surface through attractive forces or chemical attachment. SAMs on the other hand achieve similar molecular films through chemical attachment of reactive molecules with surfaces through diffusion. The self-assembly is achieved through the small size of the molecules, with ordered attachment allowed by the surface reactive sites. Once the small molecules are chemically attached to surfaces, polymers can be chemically attached the surface through a reaction with the terminal functional group of the surface tethered molecule.
Silane functional groups are by far the most utilized functional group to attach small molecules to hydroxyl containing oxide surfaces, especially silica surfaces, which are one of the most well-studied surfaces in the general area of surface modification. The attachment strategy utilized by silane chemistry is the same when producing silicon oxides, where alkoxy silanes hydrolyze to yield silanols and the more reactive silanol groups later condense with one another to form the Si-O-Si bond, as described in the extensively utilized Stöber process. When designing silane attachment molecules, it is important to consider the nature of the hydrolyzable groups. For example, more reactive chlorine groups tend to hydrolyze much faster than the more stable alkoxy groups, so handling of the silane molecules is very important when attempting to retain the integrity of the reactive silanes. The number of hydrolysable groups also play a large role since this factor tends to influence the surface film morphology.

Alkoxy silanes (methoxy and ethoxy silanes) have attracted a lot of attention for preparation of silane films, due to the stability of the hydrolyzable alkoxy groups compared to the chlorosilanes, which makes the silanes easier to work with, while also producing less corrosive byproducts (alcohols instead of HCl). When considering the number of alkoxy groups on the attaching molecule, there appears to be an obvious affect over film morphology. Each alkoxy reactive groups has the opportunity to react with one another once they hydrolyze to yield a more reactive hydroxyl group. The hydroxyl groups can then condense with one another to produce the siloxane bond in a manner very similar to the ethoxy groups of tetraethyl orthosilicate, hydrolyzing and reacting with one another during the synthesis of Stöber particles.

The coupling between the silanols forms siloxane bonds between adjacent silane molecules and may continue, linking many silane molecules together, forming network structures, otherwise known as aggregates. The formation of these functionalized aggregates still has the opportunity to react with surface hydroxyls to produce surface bound aggregates (Figure 2.3). One example of the formation of relatively large aggregates was studied for surface modification using
aminopropyl triethoxysilane (APTES).\textsuperscript{50, 51} Attachment of APTES molecules is achieved when an excess (relative to the number of surface reactive sites) is dissolved in dry toluene and is exposed to the surface where surface modification is desired. The solution is then heated near reflux, where the high boiling point of toluene allows for the formation of the desired silanols and removal of the condensation by-product water. This study, published by Shircliff and coworkers, employed atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to study the formation of amino functionalized silicate aggregates on silicon surfaces under deposition times of up to 19 hours using the triethoxysilane functionalized APTES.\textsuperscript{50, 51} Shorter reaction times of one hour produce smaller aggregates, while at longer reaction times (19 hours), the aggregates grow and deposit to produce quite large surface structures (Figure 2.3).

![Figure 2.3](image-url)

**Figure 2.3.** Atomic force microscopy results of films produced from aminopropyl triethoxysilane (APTES), along with a cartoon depiction of what the large aggregates are made of and how the tri functionality can be used to produce the aggregates. Figure adapted and modified from 50.

An envisioned way to prevent the production of large aggregates was to use a silane with one or two hydrolysable groups, due to the limited number of connections between molecules that would be possible. Monoalkoxysilanes would only produce dimers when coupled with one another in solution and difunctional silanes would produce polymeric siloxanes. Instead of aggregates
formed by the mono and difunctional silanes, the much simpler structures can couple with the surface to produce single monolayers in the case for the mono functional silane and tethered polymeric structures in the case of the difunctional version. In the SAM study performed by Shircliff et al., the same experiments as performed for APTES were conducted using (3-aminopropyl) dimethylethoxysilane (APDMES), a monoethoxysilane. The resulting film produced a more uniform attached silane layer with limited numbers of aggregates, which is what would be expected (Figure 2.4).

![APDMES](image)

Figure 2.4. AFM profiles of both plasma cleaned silica and aminopropyl silane-functionalized surfaces, demonstrating that there is no apparent change in surface morphology, with an average roughness of 0.5 nm. Figure adapted and modified from 50.

It is apparent that small molecule silanes are an effective and widely used technique for the attachment of functional groups to oxide substrates and the number of attachments on the silane control the morphology of the deposited silane film. Silane attachment strategies are not the only method utilized to covalently attach molecules to surfaces and the method used strongly depends on the nature of the surface. Other examples of linkers used for the attachment of functional
groups to surfaces include, but is not limited to: thiols for attachment to gold surfaces, attachments to metal oxides using esters, and attachment of unsaturated groups to silicon surfaces using ultraviolet activation.

Once a surface is modified with a small molecule layer, the organic functionality can be used to attach other desired materials, such as other small molecules or polymers. Some examples of chemically attaching polymers to different surfaces includes attachment of poly(ethylene glycol)s with amino end groups to surface bound succinimide ester groups, attachment of polystyrene to benzophenone groups covalently bonded to iron surfaces using electrochemical reduction of the diazonium salts of benzophenone, and photochemical attachment of polystyrene and poly(ethyloxazoline) to silica substrates functionalized with a benzophenone derivatives. It has been shown that the attachment schemes and chemistries vastly affect the polymeric film morphologies of surface-attached films. Grafting of polymers via the end group to such surfaces through various techniques discussed in the next section have the opportunity to improve the functionality and applications of tethered polymers through the use of polymer brushes.

2.3 Polymer Brushes

A polymer brush is a term that defines a specific type of polymeric coating that consists of a close arrangement of polymers covalently grafted to a surface. Two different mechanisms can be utilized to make polymer brush structures and each process is defined by the method used to attach the polymer chains to the surface. The first method is the grafting to process, where polymer films are formed when a reactive end group of a premade polymer chain reacts with, and attaches to, a functional group on the surface (Figure 2.5). Typically, the reaction between the polymer and the surface occurs through an already surface bound reactive molecule, such as silanes with terminal reactive groups, but polymers with thiol end groups can also be grafted to gold substrates.
The grafting to method can be a powerful technique because it employs preformed polymer chains that can be properly synthesized and characterized before they are attached to the surface. It can be difficult to achieve thick, uniform films and dense films when the grafting to technique is used, however. Issues surround the attachment process, where the amount of chains per unit area or the “grafting density” tends to be quite low, due to steric blocking of the surface as chains attach to the surface. The larger the molecular weight of the polymer desired to be attached, the higher the radius of gyration, and the lower the grafting density due to the steric blocking of the surface-bound reactive sites. While the lower grafting densities produced using the grafting to technique make the formation of true polymer brushes more difficult, it remains to be an effective surface modification technique for various applications where certain control over film properties is required.

The grafting from technique differs from the aforementioned grafting to method by producing the grafted polymer in-situ, where the polymer is grown from initiator molecules immobilized on the surface, to produce a much more dense arrangement of grafted polymers. Figure 2.5 compares the physisorption process to the two methods used to produce the covalently attached polymer films. The main difference between the films produced with these two methods is the grafting density and film morphology.

Polymer brushes produced using the grafting from technique overcome the issues inherent with the grafting to technique, by forcing the polymer chains to be much closer to one another. The higher grafting densities are achieved by growing the polymers from the surface using surface bound initiators. This is achieved by first chemically modifying a surface with an initiator molecule and then exposing the surface to monomer solution. The chemically bound initiator then is allowed to grow polymers from the surface with sequential monomer addition (Figure 2.5). The benefits of the grafting from method have allowed for research to focus on such an alternative
technique to produce polymer brushes. Further examples explaining how the grafting process is achieved is covered further with chain growth polymer brushes.

Figure 2.5. Contrasts between physisorption, grafting to, and grafting from techniques for polymer film formation. The stars represent the reactive end groups of the polymer where the monomer (M) adds.

2.3.1 Polymer Brush Preparation

As research continued to focus on the use of the grafting from technique for the preparation of polymer brushes, it became evident that polymerization methods based on the chain growth mechanism would be essential in order to produce films with controllable and uniform thicknesses and with the potential to make complex architectures. The grafting from process requires the polymerization method to adopt a chain growth method, where monomer adds to the end of the polymer chain in sequence. Initial research on the preparation of polymer brushes concentrated on chain growth polymers, chosen from the common list of polymers produced using vinyl monomers and conventional radical polymerization techniques. Many of the first polymer brush systems were prepared using uncontrolled methods, where surface-bound initiators would generate surface-bound radicals and add monomer sequentially to make brushes with impressive thicknesses and in relatively short times.\textsuperscript{65, 66} An example of this reaction is portrayed in Scheme
2.1, where surfaces are modified by the deposition of azo-based radical initiators onto silica or gold substrates using the monochlorosilane or thiol functional group, respectively. The uncontrolled radical polymerization is achieved when the modified surfaces is exposed to a monomer solution and the initiator is thermally or photochemically activated and a surface bound radical is formed.\textsuperscript{65, 67, 68} The issue with this process, which was realized rather quickly, is that, control over polymer brush thickness (defined by the molecular weight of the polymer), architecture, functionality, and end groups is difficult to obtain using uncontrolled radical polymerization methods.\textsuperscript{3, 69} In addition, this process tends to result in polymers with broad molecular weight distributions, which leads to non-uniform film thicknesses. The reason why uncontrolled radical processes are not ideal when preparing well defined polymer brush films, is that a high surface concentration of propagating radicals have the potential to couple with one another, thus terminating the reaction. In addition, the very fast polymerization rates and the inherent presence of termination reactions make the preparation of polymer brushes with controlled thickness difficult.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme2_1.png}
\caption{Scheme 2.1. Reactions involved with depositing an azo-based thermal initiator onto silica or gold surfaces, along with the uncontrolled radical polymerization process to produce polymer brushes via the grafting from technique.\textsuperscript{65, 67, 68}}
\end{figure}
As such, a more controlled and living procedure was required to produce polymer brushes that would exhibit reproducible brush films with more desirable properties, functionality, and architectures. Certain controlled chain growth methods allow for the potential to have a living system, where the end of the polymer can be reinitiated to add multiple blocks to the polymer brush, allowing for complex architectures. The inherent reactions in the radical polymerization process results in polymer chains initiating, propagating, and terminating over very short time periods. As consequence of this, polymer chains initiated at different times during the polymerization are exposed to different monomer concentrations and, therefore, grow to different molecular weights, which results in broad molecular weight distributions. In comparison, the more living and controlled radical processes achieve control by utilizing an activation and deactivation cycle to regulate the concentration of active radicals relative to dormant chains through an exchange process. These processes were developed to gain “control” over the polymerization by being able to synthesize polymers with desired molecular weight and a narrow molecular weight distributions.\textsuperscript{1, 2} Living polymers, a term sometimes confused with controlled polymers, are typically achieved when the polymer has the capability to reinitiate, meaning the end group remains active towards the addition of new monomer.\textsuperscript{70} Controlled-living polymers were an improvement upon their uncontrolled cousins and have become a focus for polymer research to this day for the development of polymers with unique new properties that extend from the formation of block copolymers and polymers with improved functionality. In addition, polymer brushes research has focused on the use of controlled/living polymerization techniques, due to the impressive control over the brush films that can be achieved.

2.3.2 Controlled-Living Polymerization Techniques and Subsequent Brushes

Ever since the discovery of controlled living radical polymerization (LRP) techniques, the field of advanced polymer synthesis has expanded to include a wide variety of polymers and architectures. Controlled LRP techniques employed for solution polymerizations are well studied
The most common LRP techniques used today are reversible addition-fragmentation chain transfer (RAFT) polymerization, atom transfer radical polymerization (ATRP), and nitroxide-mediated polymerization (NMP). The concept behind controlling a typically chaotic radical polymerization technique is the introduction of an activation/deactivation cycle. The LRP methods use a unique balance between the active propagating radical and unreactive chain end group using either halogens (employed by ATRP), chain transfer agents (RAFT), or nitroxide (NMP) to reversibly deactivate the polymer chain. Both of these very commonly used techniques have allowed for vinyl polymers to be produced with outstanding control over molecular weight, narrow molecular weight distributions, the ability to control functionality and architecture through the use of end group reinitiation, and the potential to create more advanced polymers.

It became apparent that the polymer brushes being produced using conventional radical polymerization techniques would benefit from the adoption of LRP techniques due to the potential that these systems could provide to the brush community, through control over thickness, functionality, and architecture. Some of the earliest examples of controlled-living polymer brushes were produced using ionic polymerizations, such as anionic and cationic surface-initiated polymerizations. Even though ionic techniques demonstrated that polymer brushes could be produced in a controlled and living manner, the stringent conditions required to maintain control over the polymerizations including very cold temperatures, no tolerance for impurities, and limited monomer selection forced chemists to look to other controlled techniques to make brushes.

Some of the first examples of LRP brushes were obtained by using the nitroxide-mediated polymerization approach. Difficulties with the NMP approach from surfaces led researchers to realize that the RAFT and ATRP techniques could also be used to prepare brushes with varying functionality from a number of different surfaces. The more versatile LRP techniques overcame the issues inherent with the problematic polymers produced using ionic methods by
creating polymers using relatively more lenient conditions by applying LRP techniques to surfaces. The first examples of brushes produced from LRP techniques were performed by tethering either an ATRP initiator (for ATRP) to the surface and expose it to a polymerization solution or in the case of RAFT, attachment of radical initiators, with a later evolution into attaching chain transfer agents, to the surface.

There are very few examples of polymer brushes obtained from non-vinyl-based monomers as this is the primary functional group needed for the techniques listed above. Ring opening metathesis polymerization (ROMP) is an example of a technique that has been demonstrated to be successful in producing polymer brushes, where monomers with alkene functionalities are necessary, but are not limited to traditional vinyl monomers, and typically involves the use of cyclic alkenes. The examples of successful surface-initiated and controlled polymerizations listed above have proved that polymer brushes can be obtained using more controlled techniques and have allowed for the production of brushes that exhibit more versatility and functionality due to their living character.

More specifically, in the case of surface-initiated RAFT polymerization, an example of successful brush growth was demonstrated by Yuan and co-workers, where a RAFT agent was attached to an aminopropyl functionalized silica surface using the reactive succinimide ester functionality (Scheme 2.2). After the RAFT agent was attached to the surface, the modified substrate was then exposed to a polymerization solution containing a radical initiator, azobisisobutyronitrile (AIBN), and monomer, in this case methyl methacrylate (MMA). The subsequent surface-initiated RAFT polymerization allowed for the production of poly(MMA) brushes with well-defined molecular weight properties.

In the case with brushes produced using ATRP, the process is similar, in that the molecule responsible for initiating the chain growth polymer is attached to the surface. However, ATRP is a different LRP technique, in that it uses halogen atoms, a redox reaction, and a persistent radical
in the activation/deactivation mechanism, with the aid of a metal center, typically copper, to receive the abstracted halogen and generate the propagating radical. The balance of activated/deactivated species allows a certain amount of active polymer chains to be exposed to the monomer solution, where the polymer is allowed to grow. It is important to control the relative activation/deactivation cycle to maintain a low concentration of active radicals, which in turn minimizes termination reactions and produces a living polymerization.

Scheme 2.2. Example of surface-initiated RAFT polymerization using succinimide activated RAFT agent attached to aminosilane self-assembled monolayer to produce a poly(methyl methacrylate) (PMMA) brush.\textsuperscript{87}

One example of how controlled brushes can be achieved using ATRP was demonstrated by Boyes et al. who produced polystyrene brushes by attaching an ATRP initiator functionalized with a chlorosilane attachment moiety to a silica substrate (Scheme 2.3).\textsuperscript{94} After attachment, the brush was synthesized by immersing the initiator-modified substrate into a styrene solution that was allowed to undergo ATRP.\textsuperscript{94} In this particular study, the brushes were reinitiated to grow a second polyelectrolytic block, to achieve multifunctional polyelectrolyte block copolymer brushes.
It has also been shown in literature that a combination of LRP techniques can be used by growing one block of a polymer brush using ATRP and then switching to RAFT to grow the second block by attaching a RAFT agent to the terminal bromo group.95

2.3.3 Random Coil Polymer Brushes: Governing Structure and Properties

The functionality of conventional polymer brushes varies widely and depends upon the nature of the polymer that was synthesized and is typically defined by the sidechain chemistry of the monomer. The structure of conventional vinyl-based polymers, however, stems from the flexibility of the sp³ hybridized carbon-carbon backbone. This flexibility instills a random structure that resembles cooked spaghetti and is properly described by the term, random coil. These random coil polymers, when attached to surfaces, can adopt a variety of structures and morphologies that depend on the spacing between chains, a term defined as grafting density. Typically, the grafting density is the primary factor in determining if a polymer brush structure is formed on a substrate and is defined by how close the attached chains are to one other or the number of attached chains per unit area.² With very low grafting density regimes or in the case of physisorption of the polymer to the surface, if the polymer has a high affinity for the surface it is considered to be in the
“pancake” regime, where the polymer spreads out to cover a relatively large area due to favorable interactions with the surface, much like a pancake in a pan (Figure 2.6). When a polymer is grafted to a surface by an end group and has very little affinity for the surface, with a moderate grafting density range (up to 0.05 chains/nm$^2$), the attached polymers become part of the mushroom regime. In this case the attached polymers tend to not interact with neighboring polymers, due to the lower grafting density, and produce a surface-tethered random coil that can be envisioned as “mushrooms” emanating from the surface (Figure 2.6). Due to the difficulty to produce films with any appreciable grafting densities through physisorption or by using the grafting to method, the majority of structures achieved via these two methods are either the pancake or mushroom structures.

When the grafting density is increased to a critical value, approaching 0.07 chains/nm$^2$ for random coil brushes, the attached polymer chains will begin to interact with neighboring chains and compress the random coil to elongate from the surface forming more a brush-like structure. The relationship between grafting density and thickness has been determined experimentally, where grafting density was varied and the thickness was measured for random coil polymers. The grafting density ($\sigma$) of a surface modified with polymer chains is determined through the following equation,

$$\sigma = \frac{\text{number of chains}}{\text{unit area}} = \frac{h \rho N_A}{M_n}$$

(2.1)

Where $h$ is the thickness of the polymer film, $\rho$ is the density of the polymer, $N_A$ is Avogadro’s number, and $M_n$ is the number average molecular weight of the polymer. The specific scaling relationships for the brush thickness in the mushroom and brush regimes are as follows,

$$H_m \sim a \left(\frac{N}{\sigma}\right)^{1/2} \sim N \sigma^0$$

(2.2)
\[ H_b \sim N \sigma^{1/3} \]  

where the polymer chains consist of \( N \) statistical segments of diameter \( a \), and \( H_m \) are is the thickness of the mushroom film and \( H_b \) is the thickness of the brush film.\(^1\) If the attached polymers are in the brush regime, the thickness increases with increasing grafting density (to a power of one third), due to the steric interactions between chains that force the chains to adopt a more of an elongated state, due to the compressed random coil of the brush structure (Figure 2.6).\(^{97,98}\) It is also apparent in the relationships above, for surface attached polymers in the mushroom regime, the thickness scales with a grafting density to the power of zero or, in other words, the thickness is independent of grafting density.

![Three conformations of polymers](image)

Figure 2.6. The three conformations polymers can adopt when attached to a surface.

Despite these differences, it is important to note that the structure of the polymer films remain a random coil, even though they are considered to be elongated in the brush form and unaffected in the mushroom formation. The random coil structure can, and have been shown to have very useful stimuli-responsive properties, where films respond to an external stimuli to produce surfaces with multiple properties.\(^{95,99,100}\)
2.3.4 Limitations of Conventional Random Coil Brushes

As mentioned previously, the polymers employed in the majority of polymer brush research are produced using a variety of LRP techniques and involve monomers containing the vinyl functional group. As such, the resulting polymer consists of a flexible aliphatic backbone and the majority of the polymer’s functionality comes from the chemistry of any pendant groups present. The highly flexible random coil structure allows for a variety of different properties, such as stimuli responsive systems, where the structure of the particular brush film can change thickness or phase separate on the surface when composed of block copolymers to exhibit interesting properties. The random and flexible backbones, however do not have the ability to exhibit the properties that arise from polymers with more rigid backbones with higher degrees of ordering. Polymers with more rigid character exhibit different properties by having more elongated backbones that have the ability to interact with one another. When polymers with more rigid and elongated backbones are grafted to substrates, they offer the potential to exhibit favorable tribological properties, improved transport along aligned chains, and the potential for high performance composites used for high-strength applications.

Some of the most versatile materials that exhibit high-strength and high temperature applications tend to be polymers. Some well-known examples that industry commonly uses are Kevlar® and Nomex®, due to the unique properties that polymers possess when compared to their inorganic counterparts. One of the main reasons why these polymers are able to exhibit these advantageous properties comes from the chemical makeup of the polymer backbone. Typically, high performance polymeric materials consist of polymers that are composed of more elaborate backbones containing stiffer, and more typically aromatic repeating units with bonds that consist of heteroatoms such as esters, amides, carbonate, and silicone linkages to name a few. The one main difference between the synthesis schemes required to produce condensation polymers and the more conventional vinyl polymers is that condensation polymers
typically require a step growth process. This process does not benefit from the advantages that controlled chain growth processes provide, such as the ability to create advanced architectures, controlled molecular weights, narrow molecular weight distributions and to produce controllable polymers via the grafting from method.

2.4 Chain Growth vs. Step Growth Polymerization Techniques

Controlled chain growth processes, such as the LRP techniques, rely on the sequential addition of monomer to the end of the polymer chain in a systematic manner. With this process, if termination reactions are limited, the molecular weight grows linearly with conversion (Figure 2.7). Step-growth polymers on the other hand, produce polymers by a more statistical process, where monomers react with one another in a “stepwise” fashion to produce molecules with gradually increasing molecular weight, slowly at the beginning of polymerization and with the assembly of the larger molecular weight polymers towards the end of the polymerization (Figure 2.7).\textsuperscript{69, 106} The step growth process achieves its status typically from the condensation reactions between monomers that have dual functionality. Typical step-growth polymers employ the reactive functional groups to steadily grow oligomers until appreciable sized polymers are formed when the larger oligomers begin to couple with one another to reach statistical molecular weight distributions with the polydispersity index (PDI) approaching two.\textsuperscript{69} When examining the relationship between molecular weight and conversion for step-growth polymerizations it is apparent that large molecular weights are only achieved near high conversions (Figure 2.7). Most applications that utilize polymers made via this process do not require control over the polymerization or the desire to produce block copolymers, due to the satisfactory and impressive properties that the majority of polymers possess using the step growth method.

With conventional, uncontrolled chain growth polymerizations, the inverse of step growth polymerizations is observed, in that, high molecular weight polymers are produced rapidly at fairly low conversions and the average molecular weight tends to reach a limit (Figure 2.7) from
termination mechanisms and begins to slightly decrease. The reduction in molecular weight comes from to the reduction in monomer concentration at high conversions and the fact that initiation occurs throughout the polymerization. The molecular weight evolution with conversion for controlled chain growth methods, when compared to conventional chain growth and step growth, reveals why controlled chain growth is the technique of choice when producing well-defined polymers (Figure 2.7). The minimization of termination reactions in controlled chain growth polymerizations provides excellent control over the molecular weight, with a linear relationship between conversion and molecular weight.

![Figure 2.7. Molecular weight versus conversion for the three main polymerization techniques utilized to produce polymers.](image)

### 2.4.1 Condensation Polymers: Potential to Produce Different Backbones

As discussed previously, most chain growth polymerizations employing vinyl monomers produce aliphatic carbon-carbon backbones with flexible behavior. The functionality of the polymer stems primarily from the pendant groups attached to the backbone and these particular
polymers are typically not well known for many high performance applications due to their more flexible random coil structure that has the tendency to not crystallize.

The discovery of polymers that exhibit impressive physical and chemical properties, typically as a result of rigid aromatic backbones and strong intermolecular forces, and are suitable for many high performance applications. Rigid rod polymers, when spun into fibers tend to align along the axis of the fibers and allow the strength of the fiber to benefit from the rigid polymer backbones through interactions between one another. The intermolecular interactions between chains and rigidity along the backbone allow for resistance to creep in materials, caused by polymer chains sliding past one another, which would lead the material to deform or decompose much easier.¹⁰⁵ Arguably, one of the most well-known classes of high performance materials are poly(aromatic amides) or aramids, with specific examples employed by industry being Kevlar© and Nomex©.¹⁰⁷ Kevlar© is produced using the condensation reaction between an aromatic amine and aromatic diacid chloride using a step-growth polymerization approach (Scheme 2.4). The key points when considering the polymerization of Kevlar© is that the extremely electrophilic carbonyl carbon in an acid chloride is very susceptible to nucleophilic attack and reacts quite readily with free amines. The equal reactivity of both functional groups on both monomers means the condensation reactions will occur randomly in a step growth manner.

![Scheme 2.4. Production of Kevlar©, where phenylene diamine reacts with terephaloyl chloride in a step growth process to form one of the toughest polymeric materials known.](image-url)
The rigid aromatic backbones with the very strong hydrogen bonds between chains account for the impressive strength of the aligned fibers and thermal stability of materials composed of the aramids such as Kevlar©. Aromatic polybenzamides also have been shown to exhibit to control conductivities of charged species using sulfonate groups along the rigid backbone.

Aromatic polyimides are also very impressive materials, due to the stability of the imide bond, coupled with the rigidity of the aromatic backbones of the repeating monomers. One commonly used polyimide is Kapton®, a polymer produced using a step growth process between an aromatic diamine, 4,4'-oxydianiline and a dianhydride, pyromellitic dianhydride (Scheme 2.5). After ring closing step, where the acid and amide that resulted from the initial reaction forces a ring closure to drive off water and produce the aromatic polyimides.

![Scheme 2.5](image)

Scheme 2.5. Production of a common polyimide, Kapton, where 4,4'-oxydianiline reacts with pyromellitic dianhydride in a step growth process to form a high performance polyimide.

There are a number of limitations with producing condensation polymers via the step growth process, including the inability to produce controlled block copolymers, the difficulty in preparing surface grafted controllable films, and the polymers produced typically have lower molecular weights and relatively broad molecular weight distributions. Recent research improving upon conventional step growth polymers has discovered that many traditional condensation polymers can be produced using a chain growth method, thus allowing for better control over the
polymerization by preparing polymers with defined molecular weights with narrow molecular weight distributions.

2.5 Chain Growth Polycondensation: Revolutionizing Condensation Polymer Synthesis

Ever since controlled/living chain growth polymers provided a means to produce polymers with improved functionality and advanced architectures, such as polymer brushes and block copolymers, there has been a desire to produce condensation polymers in a controlled manner. The ability to produce condensation polymers via a controlled chain growth process would allow for the formation of block copolymers or surface bound polymer brushes from polymers typically not used for these architectures, such as aramids and conjugated polymers. This would also potentially broaden the applications for these high performance materials by allowing for surface grafted composites and the utilization of block copolymers for more multifunctional roles. The foundational research surrounding the transition from conventional step growth condensation polymerization techniques to the more novel chain growth condensation (CGC) processes has been developed by both Yokozawa and McCullough and has been extensively reviewed.\textsuperscript{4, 5, 112-115} The main concept behind converting a step growth process to chain growth is ensuring that the monomer preferentially reacts at the growing end of the polymer chain, as opposed to a random processes, where all functional groups have an equal probability to react with one another.

There are two main processes that have been developed to produce CGCs. The first example is activation/deactivation using the substituent effect (Figure 2.8A) and the other is intramolecular transfer of a catalyst (Figure 2.8B).\textsuperscript{113} Overall, in both systems the chain growth process is achieved by encouraging the monomer to react with the end of the chain. The two main processes utilized to achieve CGC will be covered in more detail in upcoming sections.
2.5.1 Chain Growth Polymerization via the Activation/Deactivation Method

One way that CGC can be achieved is through an activation/deactivation process. When the reactive end groups of the initiator or polymer are activated towards reaction with a monomer and the monomer is deactivated towards reaction with other monomers, addition will preferentially occur at the end of the growing chain (Figure 2.8A). This can be achieved through the use of substituent inductive effects typically observed on aromatic rings. A good representation of this process is portrayed in Figure 2.9 for the synthesis of poly((N-alkyl)benzamides). In this case, substituent effects are utilized to activate the ester groups of an initiator or the growing polymer chain through electron withdrawing groups, while the electron donating group of the amide anion deactivates the ester group of the monomer preventing reaction between monomers. This difference in reactivity results in the majority of monomer condensation reactions occurring at the end of the polymer chain, forcing the reaction to proceed in a chain growth manner.

Figure 2.8. Description of the two main processes that define chain growth condensation. The first description is for the change of the (A) substituent effect, where the monomer is deactivated, resulting in preferentially addition at the more reactive polymer end group and (B) transfer of catalyst, where chain growth is achieved via intramolecular catalyst transfer, which limits monomer reactivity with the polymer end group. Figure adapted and modified from 113.
Figure 2.9. An example of how the substituent effect chain growth condensation process can be used to convert step growth to chain growth. Figure adapted from 113.

The activation/deactivation via substituent effect process is mainly explained by changing the electrophilicity of the various ester carbonyl carbons in the system. In general, the ester carbonyl carbon is considered to be activated when it is more electrophilic and deactivated when it is less electrophilic. This results in the activated ester carbonyl carbons being more susceptible to nucleophilic attack by the amide ion of the monomer. The increase in electrophilicity is achieved by placing an electron withdrawing group on an aromatic ring, which draws electron density away from the carbonyl, increasing the reactivity of the ester. The inverse is true for the deactivated ester group of the monomer, where the carbonyl carbon becomes less electrophilic via the presence of an electron donating group on the aromatic ring, making the carbonyl carbon less susceptible to nucleophilic attack. For the system portrayed in Figure 2.9, the polymerization starts with the deprotonation of the monomer at the secondary amine. The resulting amide anion, being a strong electron donating group, donates its charge via induction to the carbonyl carbon of the ester and deactivates the ester to nucleophilic acyl substitution. The amide anion is also a very strong nucleophile and is capable of nucleophilic attack on any activated ester groups, such
as the initiator or the end group of the polymer. The vast majority of monomer will preferentially add to the polymer end group, resulting in the system following a chain growth process.

The benefit of the substituent effect CGC process is twofold. The chain growth nature of this system allows for the control over molecular weight by simply varying the feed ratio of monomer to initiator and obtaining the desired molecular weight at a particular conversion. Due to the lack of termination mechanisms possible with GCG via the activation/deactivation method, polymers with defined molecular weights can be produced with 100% conversion. The true living character of polymers produced using this method also allows for addition of new monomer to continue the polymerization again to produce more advanced polymer structures.

The availability to gain control over the polymerization using substituent effects has allowed for the production of well-defined aramids with varying functionality. For example, due to nitrogen’s available three bonds, the amide bond contains one extra bond for substituent groups that can contribute to the functionality of the aramid. High performance polyamides mostly are composed of secondary amides, where the third bond on nitrogen contains a hydrogen and the materials mostly derive their properties from hydrogen bonding between the rigid chain backbones. The rigid backbones and attractive forces between chains contribute to the high strength of the materials, the resistance to decomposition at high temperatures, and the chemical resilience. However, the presence of these strong intermolecular forces is why such materials are very difficult to produce in common organic solvents, due to their very poor solubility in those solvents. Even though the excellent performance of functionalized aramids can be reduced through functionalization by replacing the hydrogen on the amide with another functional group, there remain benefits of making the polymer more soluble, by being able to produce and processes the polymers in solution.

Yokozawa and coworkers have been at the forefront of the research creating polybenzamides via the substituent effect CGC technique and have been able to create some very interesting
polymers using this method. The majority of polymers prepared in the early studies on substituent effect CGC contained an octyl chain on the nitrogen, due to the success achieved in producing more soluble polymers with appreciable molecular weights and narrow molecular weight distributions with this monomer. Even though the polymers produced had good solubility in common solvents, the non-polar octyl pendant group provided little functionality and the overall mechanical properties of the polymer obtained were not impressive. As such, other polymer architectures and functionalities, such as aramids containing more hydrophilic character using triethylene glycol (TEG) sidechains, were envisioned to allow these polymers to interact with more polar media. Block copolymer aramids containing both the octyl and TEG side chains were produced by first making the octyl containing polymer and then introducing the TEG monomer, and was possible due to the living nature of the polymer (Scheme 2.6).

![Scheme 2.6](image)

Scheme 2.6. An example of a block copolymer with varying amide substituents that have produced multifunctional polybenzmides via the chain growth condensation method.

The impressive properties of poly(aromatic amides) is the main reason for interest in polyamide research and the desire to achieve polymers with secondary amides using a chain growth method is one of the challenges when producing aramids using CGC. The two most obvious issues with creating secondary aramids using CGC is the poor solubility of the resulting polymer and the relatively acidic amide proton that would be present on the polymer that would neutralize the base employed. To address these issues, Yokozawa and coworkers made
polyaramids using the CGC method with a monomer that contained a solubilizing protecting group on the nitrogen and, after the polymer was formed, the pendant group on the tertiary amide was deprotected to yield the more versatile secondary amide containing the hydrogen atom. The protecting group, a benzyl ether, increases the solubility of the polymer during the polymerization while also allowing for an easy deprotection approach, using a strong organic acid, trifluoroacetic acid, to cleave the benzylic group from the amide (Scheme 2.7) copolymers were also made with the soluble version to make the deprotected polymer more soluble in solution.

Scheme 2.7. A representative reaction of how a deprotecting group can be used to produce a secondary amide.

Work has also been conducted to functionalize the backbone aromatic ring to instill additional functionality to the aramid. Some of the most interesting work in this area is by Ohta et al., where the solubility of the polymer was increased by adding a solubilizing octyl group to the 3-position of the monomer, ortho to the amino group. This solubilizing group has shown to keep the polymer soluble in solution even when a protecting group on the nitrogen is used and is deprotected, yielding the more functional secondary amide that is more soluble in conventional organic solvents, such as acetone, N-methylpyrrolidone, dimethylformamide, dimethylsulfoxide, and various alcohols where the ordinary unprotected poly(p-benzamide) would have low solubility.

Once it was discovered that the aromatic portion of the aramid could be functionalized, one of the more impressive structures that have been produced using the substituent CGC technique, poly(benzoxazole), was produced. The most interesting aspect about the production of this
polymer is that it uses both an ethylene glycol sidechain on the aromatic backbone and the benzyl ether group on the amine as protecting groups. The benzyl ether is attached to the nitrogen as the deprotecting group for a secondary benzamides and the glycol ether is a protecting group for a phenol group by being attached directly to the aromatic backbone. When both protecting groups are removed, using TFA, the resulting ortho phenol and secondary amide can ring close at high temperatures to form poly(benzoazole) (Scheme 2.8), which is a unique polymer stable to very high temperatures (over 400 °C), due to its rigid ladder-like backbone. The regular arrangement of rigid polymers with the addition of favorable interactions between chains allows for the potential to produce unique structures that would be beneficial to certain high-temperature and liquid crystalline applications.\textsuperscript{122}

Scheme 2.8. Production of poly(benzoazole) using CGC polymerization. The deprotection of two groups to allow for the cyclization of the amide and ortho phenol groups.\textsuperscript{122}

As mentioned throughout the discussion of polymers prepared using the CGC method, one important advantage of using a controlled/living CGC technique is the potential to produce various types of copolymers. One particular example of how graft copolymers can be produced using a
combination of polymerization methods was the production of a composite material to improve the thermal properties of polystyrene. To achieve this, first a macromonomer derivative of styrene was produced using phenyl 4-vinylbenzoate as an initiator with a protected version of the CGC monomer (Scheme 2.9). After the CGC polymerization, the resultant macromonomer was polymerized using a conventional radical process. After production of the copolymer, the protected aramid side chains were deprotected using TFA, in a method similar to previous discussions, to produce a more thermally stable composite material than the original unmodified polystyrene system.

Scheme 2.9. An example of how two different polymerization techniques can be used to produce graft copolymers to improve the thermal properties of polystyrene.

Another class of polymer produced using the substituent effects CGC method are aromatic polyethers. For the case of aromatic polyethers, the reaction that is occurring is nucleophilic
aromatic substitution, using phenoxide anions as the nucleophile and fluoro-aromatic groups as the electrophile. This process, well understood for nucleophilic aromatic substitution, involves electron donating groups deactivating the ring towards nucleophilic addition and electron withdrawing groups activating it, alternatively. As such, when a fluoro-phenol derived monomer is deprotonated at the phenol, the resulting phenoxide deactivates the ring towards reactions with itself, thus suppressing a step growth process occurring. When a more activated species, such as an initiator or polymer chain is introduced to the mix, the reaction will preferentially occur at the end of these molecules, and the polymer will grow in a chain growth manner (Figure 2.10).

![Figure 2.10. A depiction of how activation and deactivation is used to produce aromatic polyethers through nucleophilic acyl substitution.](image)

Even though this process produced polymers with good control over the molecular weight and narrow molecular weight distributions, high molecular weights were difficult to produce, due to issues with trans-etherification, which is also a problem with the production of poly(aromatic esters) using the CGC processes.
The production of poly(para-benzoate esters) has also been demonstrated successfully using the CGC activation/deactivation technique, but control over the polymerizations remained difficult due to the problem with transesterification.\textsuperscript{127} The concept of transesterification, like trans-etherification, is when the reactive monomer species is capable of attacking the linking bonds along the polymer backbone to break the polymer into smaller pieces, which reverses the chain growth process that has occurred. It is important to suppress the side reactions if controllable, well-defined polymers are desired. One of the benefits of growing aramids, for example, is that the formed amide bond is much more resistant to side reactions than esters or ether groups under similar conditions, so well-defined polymers can be achieved using the CGC process.

2.5.2 Chain Growth Condensation via Catalyst Transfer Method

The other major process used to produce CGC polymers is the intramolecular transfer of catalyst for cross-coupling polymerization reactions. The majority of conjugated polymers produced today involve the use of cross-coupling reactions, between organometallic or Grignard-based aromatic monomers. The polymerization mechanism involves a coupling between monomer and polymer through oxidative addition and reductive elimination via a metal catalyst.\textsuperscript{128, 129} This process, like anywhere the monomers have equal reactivities, is typically a step growth process, where monomers couple with one another in a random fashion to produce slow-growing oligomers that eventually couple with one another to produce high molecular weight polymers. The CGC technique via catalyst transfer, like the substituent effect, is performed when the monomer preferentially reacts with end of the growing chain rather than react with itself (Figure 2.8B).

The discovery of the chain growth process for these specific reactions has drastically changed the control that can be obtained over these polymers. The chain growth process was originally discovered by McCullough et al., when, under certain conditions, regioregular polythiophenes were produced using a nickel catalyst with narrow molecular weight distributions and degrees of
polymerization approaching the loading ratio of the monomer to catalyst.\textsuperscript{130-132} This initial work discovered that control over the polymerization would occur without the addition of an initiator, so the proposed mechanism involved first the production of a dimer between two thiophene monomers that would then act as an ‘initiator’ for the subsequent polymerization. Recent advancements in the development of CGC via catalyst transfer involve the use of an external initiator to grow the polymers in a chain growth manner. An advantage of this approach is that the initiator-defined end group functionality can make these conjugated polymers more versatile by allowing for a series of post-polymerization reactions. Externally initiated polythiophenes have attracted considerable attention, due to the increased end group control that is available, along with the ability to potentially grow thiophenes from surfaces using a surface-initiated CGC process.\textsuperscript{133-135}

The idea of externally initiated thiophenes revolves around the use of an activated initiator by placing the catalyst on the end of the initiating molecule, ready to react with an incoming monomer. For Example, Bronstein et al. prepared an activated external initiator by mixing a reactive homogeneous nickel catalyst with an aryl halide. The dichloridobis(triphenylphosphane)nickel (II) catalyst can then oxidatively add between the aryl halide, which loads the catalyst on the initiator substrate.\textsuperscript{133} After a ligand exchange with 1,3-bis(diphenylphosphino)propane (dppp) to replace the more reactive ligands with one that helps to control the reaction better, the reactive initiator is then ready to react with monomer, and the CGC occurs with the addition of the Grignard monomer (Scheme 2.10).

The proposed mechanism for the demonstrated chain-growth behavior is that instead of completely ejecting the metal catalyst during the reductive elimination stage to yield a free metal/ligand complex, the catalyst would “walk” across the pi system of the newly added monomer to oxidatively add to the end of the chain, keeping the end of the chain as the “active site.” If the catalyst would instead reductively eliminate to the free metal/ligand complex, it would oxidatively
insert into a new monomer in a statistical manner and a step growth process would dominate. This process, called catalyst walking, has been reviewed extensively for the Kumada coupling reaction, and is also portrayed in Scheme 2.10 for the synthesis of regioregular poly(3-hexylthiophene) (P3HT) using an external initiator.

Scheme 2.10. Catalyst transfer mechanism for the synthesis of P3HT using the chain growth condensation technique.

The results of the external initiator studies have demonstrated that polythiophenes can be externally initiated resulting in polymers with the desired end groups. This end group control allowed for the production surface initiated conjugated polymer brushes (covered in section 2.6.2) and the development of various copolymers through sequential polymerizations. Examples of copolymers produced for specific energy-related applications include conducting block copolymers used in conductive plastic electronics and polythiophene-b-polystyrene for photovoltaic applications using a combination of ATRP and Kumada-catalyst transfer polymerization methods. Polyphenylenes have also been demonstrated using the Kumada coupling reaction by Lanni and Higashihara, using similar reaction conditions to the polythiophene system, where the same nickel catalyst is used with Grignard monomers of alkoxy-substituted aryl halides.
Another catalyst transfer reaction utilized for the production of CGC was with the Suzuki-Miyaura coupling technique for the production polyfluorenes.\textsuperscript{142, 143} This reaction, much like the Kumada coupling reaction, uses a homogeneous catalyst, in this case, palladium. The catalyst oxidatively adds to the borate position of the monomer and can then “walk” across the pi system to reinsert itself between the aryl halide (Scheme 2.11). This process repeats until the monomer is consumed to produce controlled polyfluorenes via the Suzuki-Miyaura process.

![Scheme 2.11. Suzuki-Miyaura catalyst transfer mechanism for the synthesis of polyfluorenes using the chain growth condensation technique.](image)

**2.6 Rigid-Rod Polymer Brushes**

Until recently, the vast majority of polymer brush research has focused on the production of random coil type polymers produced using LRP techniques. These controlled/living techniques produce well-defined polymer brushes with controlled and uniform thicknesses, complex architectures, and various functionalities. While the use of LRP techniques has produced a wide variety of polymer brushes with exciting and new properties, the structure of the polymers on the surface are compressed random coils not fully extended polymer chains. Ever since the conception of polymer brushes, there has been interest with surface-bound polymer architectures that are composed of polymers with more rigid character that can assemble into highly ordered structures. Figure 2.11 portrays the main difference between random coil polymer brushes and brushes envisioned to be produced using polymers with a more rigid structure. Recently, interest
in surface attachment of polymers that are utilized for higher performance materials has increased, due to the discovery of the CGC processes discussed above.

Figure 2.11. Contrast between the structure of compressed random coil brushes and the potential structures of a rigid rod brush, where the rigid backbone allows for full chain extension and alignment.

2.6.1 Early Work Investigating Semi-Flexible, Rigid Rod Polymer Brushes

Interest regarding surface-bound polymer brushes comprised of semiflexible or rigid backbones began with theoretical studies.\textsuperscript{144-147} The potential new and interesting properties possible with more rigid chains that are fully, or near fully extended have begun to suggest new and interesting properties possible with these new more aligned liquid-crystalline polymer brushes.\textsuperscript{144} Liquid crystalline polymers in this case are ones that order in a crystalline manner, and do not have rigid backbones, but behave in similar ways. With these studies, it was discovered that these rigid polymer brushes can collapse under changing external conditions, namely solvent and temperature for example. These transitions were modelled to go through a phase transition from an isotropic to anisotropic state through a collapse. These studies were
important, because they began to model polymer brushes that exhibited some sort of ordering, which led to further studies that examined polymers with more rigid character in the backbone.

Increased interest into polymers with more “semi-flexible” backbones began to gain attention by using modelling and the topic of liquid crystalline polymer brushes became a focus of interest, due to the more oriented chains that resulted from the simulations.¹⁴⁷ For polymers to achieve these properties the stiffness of the chain must be relatively rigid the density of chains must be large. These properties were observed without any interactions between chains, and when interchain attractions were added, the effect was dramatically increased.

More recent studies examined polymer brushes with semi-flexible character by modelling polymers with semi-flexible backbones end grafted to a repulsive planar substrate under good solvent conditions.¹⁴⁸ The studies looked at scaling behavior and brush structure using computer simulations and self-consistent field theory by changing the persistence chain length and grafting density. According to Egorov, unlike a flexible, random coil mushroom, which has self-similar structure from the size, a semiflexible mushroom exhibits three different scaling relationships, due to the weaker excluded-volume interactions.¹⁴⁸ In this case there occurs an additional regime where semiflexible mushrooms overlap without significant chain stretching. With this, the size of semiflexible mushrooms are much larger than a flexible mushroom with the same persistence length, the crossover point occurs at much smaller grafting densities than fully flexible chains and higher grafting densities than flexible brushes are possible.

The lessons from these studies demonstrate that polymers grafted to an impermeable surface with more rigid character are able to pack at much higher grafting densities and tend to interact with one another more intimately than random coil brushes. These high density polymers with more aligned character show promise when designing materials that require a higher degree of ordering used in high performance applications.
2.6.2 Conjugated Polymer Brushes

Conjugated polymers are a very interesting field of polymer research, due to the novel electronic properties that ordinary polymers are not able to provide. Conjugated polymers are polymers consisting of alternating conjugated bonds that have the ability to carry charge or even respond to electric fields, due to the alternating double and single bonds that allow for multiple mechanisms of charge transport.\textsuperscript{149, 150} The concept of creating conjugated polymer brushes on surfaces has recently drawn attention from a number of research groups, due to the potential to align otherwise random arrangements of polymers, so the electronic mobility properties of the polymer film can be improved. Charge transport is well understood for bulk films, and has been shown to happen along the chain backbone with the most ease. As such, it has been hypothesized that charge transport would occur much easier if the polymer chains were aligned normal to the surface of interest,\textsuperscript{149, 151-153} and the alignment of conjugated polymers normal to the surface with covalent attachment has the opportunity to increase charge injection efficiencies (Figure 2.12).\textsuperscript{154, 155} Issues, however, with preparing these systems has made their realization very difficult.\textsuperscript{156}

![Figure 2.12. A cartoon depiction of how oriented polymer brushes can be used to direct and improve charge transport in an organic solar cell device using polymer brushes. Figure adapted from\textsuperscript{157}.](image-url)
Attempts to produce the desired surface-bound conjugated polymers begun with the concept of surface grafting using conventional step growth methods with surface bound monomers. There have been a few examples of surface grafting via the step growth condensation polymerization technique but results from these studies yield films that are uncontrollable and very undefined, due to the random polymerization process of creating oligomers in solution and subsequent attachment of the oligomers and monomers to the surface. There were issues with attempting to surface grafting of polyfluorenes using the step growth process and no appreciable results were achieved using this surface grafting method, with only small increase in thickness (~5 nm) and a scattered arrangement of attached oligomers on the surfaces detected.\textsuperscript{158}

A second slightly more successful approach has been to first growth the conjugated polymers in solution and then to end-graft them to the surface using the grafting to strategy. This method provides the ability to characterize the premade polymers before attachment, so the properties of the polymer were well-defined. Examples of this method include attachment of thiol end-functionalized polyacetylene to a gold surface,\textsuperscript{159} amino end functionalized polythiophene attachment to quantum dots nanocrystals for solar cells,\textsuperscript{160} utilization of click chemistry to attach P3HT to ethynyl modified silica, \textsuperscript{161} and poly(phenylene ethynylene)-type polymers grafted onto silica nanoparticles.\textsuperscript{162} Despite these studies demonstrating that the grafting to method allows for attachment of conjugated polymers to surfaces, the results obtained demonstrated that these systems also suffered from the limitations of the grafting to technique using random coil polymers. For example, in each case the grafting densities achieved were quite low and it was difficult to control the film morphology and structure, due to the difficulty for reactive groups to attach to surfaces that are blocked by neighboring polymers. The rigid rod backbones of conjugated polymers would theoretically allow for increased grafting densities via the grafting to method, due to the more tapered profiles of the more elongated chains, but difficulties with increased
interactions between chains through pi-pi interactions making the grafting to process very
difficult.\textsuperscript{159, 161}

The CGC polymerization techniques discussed above have the potential to have a profound
impact on the production of rigid rod polymer brushes, due to their ability to convert step growth
processes to chain growth, providing the overall requirement of using controlled/living chain
growth processes to produce well defined polymer brushes via the grating to technique.

2.6.3 Surface-Initiated Chain Growth Condensation Polymerization

The innovative Kumada coupling reaction has been recently reviewed by Luscombe and Kiriy
and has been shown to produce conjugated polymer brushes by developing a way to synthesize
polymers from an external initiator in solution.\textsuperscript{136, 163} The first and only concrete examples of
surface initiated rigid rod polymer brushes has been from work producing chain growth conjugated
polymer brushes via the catalyst transfer CGC process using surface-attached external initiators.
One of the earliest attempts to grow conjugated brushes from a surface was the preparation of
polythiophene films from poly(4-bromostyrene) films using Kumada catalyst transfer. The
bromostyrene film was spin coated onto silicon wafers that were pre-covered with a 2 nm thick
poly(glycidyl methacrylate) (PGMA) adhesive layer and crosslinked to achieve integrity. The
initiator group, very similar to the external initiators employed in solution work, being the bromoaryl
group is attached to a polymer backbone and is bound to a surface immobilized polymer. The
structure of the initiator layer, being a crosslinked bromostyrene film has the ability to swell with
the introduction of a good solvent, and the initiators remain along the backbone of the polymer.

To effectively grow the thiophene chains from the initiators, a similar scheme to the external
initiator work was employed, where the bromoaryl groups were first loaded with catalyst, in this
case Ni(PPh\textsubscript{3})\textsubscript{4} in toluene and then polymerized by introducing the Grignard monomer in
tetrahydrofuran. Various thicknesses of bromostyrene films from 1 to 200 nm were produced to
observe the effect on the growth of the thiophene layer. Thiophene films achieved thicknesses up to 150 nm when grown a starting bromostyrene film of 100 nm.

The idealized structure of the polymer envisioned to grow polythiophene brushes from the surface of the polystyrene layer (Figure 2.13a). As a result of their findings, a more accurate depiction of the resulting surface grafted poly(3-hexylthiophene) (P3HT) is depicted in Figure 2.13b, where a more swollen interpenetrated network is probably more evident from their findings instead of the idealized brush structure. Even though the films exhibited good stability against delamination, high electrical conductivity in the doped state, and high swellability, they also proved to be promising for future applications. Future studies would shift focus to creating initiators that could be attached to impermeable substrates.

![Figure 2.13. The structure of the envisioned brush using (a) idealized brush (b) swollen network model, where the P3HT grows off the side chain of a swollen poly(4-bromostyrene) (PS-Br) layer.](image)

The discovery of externally initiated polythiophenes using the Kumada condensation process has led researchers to produce a variety of truly surface-initiated chain growth polythiophene brushes. One particular example is the production of “hairy particles” by grafting an external
initiator to silica nanoparticles with the well-known silane chemistry. A bromo aryl group was attached to silica particles via a triethoxysilane-functionalized initiator and the activated surface bound initiator was produced by loading the surface with a homogeneous nickel catalyst that goes through a ligand exchange process to prepare the surface for Kumada coupling (Scheme 2.12). Polythiophene brushes were then grown from the surface of the particles through CGC via the catalyst transfer process to produce the hairy particles by exposing the surface-bound activated initiators to the Grignard thiophene monomer.

Evidence of the thiophene brushes on the surfaces of the particles was obtained using scanning electron microscopy and obviously shows a difference before and after the brush growth (Figure 2.15). Before the brush formation, the surfaces of the particles appear to be relatively smooth with the coating of the bromo aryl silane initiator. After the surface initiated polymerization, the particles acquire a rough film that coats the particles, suggesting that polymer is attached to the surface (Figure 2.14). As reported, the initiator modified 460 nm diameter silica cores grew a shell thickness of 2 nm, obtaining polymers, when degrafted, with degrees of polymerization
approaching 250 calculated from GPC. Grafting densities calculated for these systems were calculated to be 0.28 chains/nm², suggesting a very close arrangement of elongated chains when compared to lower grafting density random coil systems. The smaller diameter particles with core diameters of 4 nm, grew shell thicknesses up to 6.5 nm with degrees of polymerization that were much smaller, reaching 24, when calculated from nuclear magnetic resonance (NMR).

Figure 2.14. Scanning electron microscopy images of the growth of the “hairy particles” after growth of P3HT from the surface.¹⁶⁸

Results from this study show a dramatic change in optical properties of solutions containing free polymer compared to the tethered counterparts as part of the hairy particles. The closely packed polythiophene chains caused a red shift and vibronic fine structure in absorption and fluorescence spectra, which was suspected to be a result of efficient planarization and chain aggregation via pi-pi stacking. This behavior was also observed by chains grafted from different diameter nanoparticles with different curvatures to change the amount of polymer aggregation.
Further research into these supported brushes have more recently been studied for sensor applications.\textsuperscript{169} These first examples of surface initiated polythiophene films have been successfully grafted from inert inorganic substrates were exciting examples of progress with the technology, the real benefits of polymer brushes were realized when polythiophene brushes were grown from electrically active substrates.

The potential to improve the hole transport layer for polymer solar cells has been mentioned previously as a motive for the application of conjugated brushes.\textsuperscript{170} The potential for aligned conjugated polymer chains normal to the surface, through a polymer brushes structure, has the opportunity to improve the hole transport efficiency. Exciting work by Doubina et al. demonstrated that thiophene brushes could be adapted to work in devices, by growing the polymer directly from the electrically active substrate, indium tin oxide (ITO).\textsuperscript{171} This process was completed by attaching a chloro aryl initiator to ITO through the use of a phosphonate ester linkage. After catalyst loading and ligand exchange, polymer was grown by exposing the surface bound initiator to the 3-methylthiophene Grignard monomer (Scheme 2.13).

Scheme 2.13. Growth of poly(3-methylthiophene) brushes from ITO substrates for applications of hole transport material layers.\textsuperscript{171}
Results from this study demonstrated that the thickness of the polymer film, for the first time could be controlled using surface-initiated Kumada catalyst transfer polymerization. Polymer thickness were regulated by the variation of solution monomer concentration and ranged from 30 to 265 nm. The films were then successfully doped through electrochemical oxidative doping to effectively tune the work function of the film. Charge transport properties were never studied for this system, however, possibly due to the issues with charge trapping and insulating chemistry that embody by the linking chemistry of the phosphonate bond and the alkyl spacer respectively.

Another example of the production of conjugated brushes is through the production of alkoxy-substituted polyphenylene brushes using the Kumada-type catalyst transfer polycondensation technique. The basic premise to produce the brushes resembles the thiophene system, where a surface bound thiophene external initiator is attached to a silica surface through the silane attachment point. The surface bound initiator then is loaded with a homogeneous nickel catalyst that subsequently goes through ligand exchange and the polymer is then formed using a Grignard aryl monomer (Scheme 2.14).

![Scheme 2.14. Production of alkoxy-substituted paraphenylene brushes via the surface-initiated Kumada catalyst transfer technique.](image-url)
Results from this study demonstrated that polymer brush other than polythiophenes could be produced using the Kumda-chain transfer and was shown to be a relatively “simple and inexpensive in terms of monomers and catalysts” for the fabrication of new conjugated thin film devices. Since these studies were only performed on flat surfaces, no molecular weight or grafting density measurements were recorded. Film thicknesses were measured to reach up to 25 nm for the unsubstituted poly(p-phenylene) films, with varying smaller thicknesses that depended on the bulkiness and length of the solubilizing group. This was also a study that demonstrated that the solubilizing group greatly affects the sterically demanding Kumada catalyst transfer technique, and has the opportunity to tune the film properties by changing the bulk or length of the side chain.

Recently, work has also begun on the production of conjugated polyfluorene brushes by surface initiated Suzuki polycondensation. Due to the relatively new discovery of use of Suzuki polycondensation process as a CGC procedure, there are few examples of creating surface grafted brushes using this technique. In one example, Beryozkina et al. grew polyfluorene brushes from crosslinked poly(4-bromostyrene) films or 4-bromo aryl initiators attached to impermeable silicon surfaces using a silane linking moiety. The process for Suzuki coupling relies on the use of a homogeneous palladium catalyst loading on to the surface-bound initiator. It is believed that the CGC process occurs through the very reactive and unusual three-coordinate palladium complex (Scheme 2.15). After exposure of the surface bound activated initiator to the bromo/borate monomer, successful CGC occurred through the Suzuki coupling technique.
Film thicknesses approaching 50 nm were measured using ellipsometry and atomic force microscopy and varied with reaction conditions mostly depending on the nature of the crosslinked bromostyrene film. Since these polymers were initiated from a crosslinked bromostyrene film, like the example given in Figure 2.13, these film produced probably takes on a swollen network of polyfluorene-grafted polystyrene. Since these films were only prepared on flat surfaces, molecular weight and grafting density measurements were not measured, due to the very small amount of polymer that is surface grafted.

As mentioned, there is a relatively small amount of research surrounding the production of surface-initiated conjugated polymer brushes and the intent of most of the studies was to only grow the polymers for certain applications, without understanding the structure and properties of the produced brushes. Even though conjugated brushes have been demonstrated to create films using the grafting from process with varying functionality, there remains a wealth of knowledge to obtain about the structures and properties of these films, where future studies can be used to understand more about these versatile structures.

To this end, no work has been observed concerning CGC brushes using activation/deactivation via the substituent effect method. The extensive range of polymers that have been demonstrated in literature to be produced using the substituent effect CGC
polymerization method in solution have the opportunity to be translated into brushes with the development of appropriate chemistries. In addition, formation of brushes from these interesting polymers has the potential to produce high performance films, due to the aligned structure and intermolecular forces that the rigid rod polymers may provide. There have been few attempts to surface graft polyaramids to and the attempts mostly involved molecular layer deposition of AA and BB monomers.\textsuperscript{174, 175} The issues with this method however, involve cumbersome sequential additions of monomers to react with surface bound reactive groups and usually involve high vacuum systems and are vapor-surface reactions.

The interest of this thesis surrounds the formation of aramid brushes using the chain growth condensation technique through the use of the substituent effect. Since the only brushes using CGC today have been produced using the catalyst transfer method, there is a huge potential for the assembly of more rigid polymer brushes through the use of the substituent activation/deactivation method. One polymerization scheme that has been covered in detail earlier is the preparation of poly(N-octyl)benzamides using the CGC technique. This polymer was chosen as an appropriate model system to develop the first examples of surface-initiated CGC polymer brushes using the substituent effect and understand the behavior of these systems.

2.7 Background Summary

Polymeric coatings have been a dominant technology used for many applications. The many processes utilized to produce these coatings range from the top down approach of applying premade polymers in solutions via spray coating, dip coating and from melt. Certain issues with these approaches can be undesirable for more demanding applications and the development of more secure attachments of polymers has led to the advent of polymer brushes with more control over structure. The evolution of polymer brushes has constantly improved the attachment strategies from physisorption where free polymers tend to weakly bond to surfaces to a more secure grafting to process where there is covalent attachment between premade polymers and
surface sites, to the implication of grafting from. The vast majority of polymer brush research today encompasses the grafting from approach that requires a chain growth polymer synthesis process. The only polymers that fit the category of controlled living polymerization techniques until recently were produced using conventional living techniques and have limited research to a very narrow class of typically vinyl polymers. The discovery of chain growth polymerization technique has allowed access to the production of more versatile polymer brushes by providing a process to assemble polymer brushes with more rigid character to produce more versatile brush films that provide coating properties that have yet to be realized.

2.7.1 Thesis Hypothesis

The hypothesis of this thesis answers the following question: Can the polymer brush field be expanded by developing novel chain growth condensation brushes using the substituent effect? With a specific answer the hypothesis reads: Because aramid polymers have been shown to be produced using an uncommon chain growth condensation method and chain growth processes are required to make well-defined polymer brushes, aramid brushes should be achievable if a proper initiator is tethered to a surface before an attempted polymerization.
CHAPTER 3
SURFACE-INITIATED CHAIN-GROWTH POLYARAMID BRUSHES

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3.1 Introduction

Polymer brushes are collections of polymers that are either physically adsorbed or covalently tethered to a surface at a high enough grafting density to force the polymer chains to adopt an extended conformation.\textsuperscript{89, 101, 176} Due to thermal and solvolytic instabilities with physically adsorbed polymer brushes, the vast amount of reported research has focused on covalent attachment of the polymer chains. Polymer brushes have been a growing topic of interest over the past two decades due to the increasing number of applications, that include ‘smart’ optical systems, microelectromechanical systems, and textiles,\textsuperscript{177} as well as the plethora of applications in the biomedical field,\textsuperscript{13} and patterned surfaces.\textsuperscript{64} Brushes can also be utilized in lubrication and protective coatings applications,\textsuperscript{178} hybrid solar cells,\textsuperscript{179, 180} colloid stabilization,\textsuperscript{100, 181} tailoring of surface electronic properties,\textsuperscript{182} and chemical gates.\textsuperscript{183} These applications utilize the unique surface structure that results from the partially extended, surface-attached polymers. The two methods commonly utilized to covalently attach polymers to surfaces are termed grafting to and grafting from. The grafting to method is when pre-synthesized polymers with reactive end groups are subsequently attached to surfaces through the formation of a covalent bond with a surface functional group. This method can be used to attach almost any polymer, synthesized using almost any technique; as long as it has a reactive group that is capable of reacting with the functional groups on the surface. The limitation of this technique is that the grafting density is typically quite low due to steric blocking of surface active sites from the attached polymers, which can affect the film uniformity and function, and makes it difficult to produce true polymer brush structures. The grafting from method on the other hand routinely achieves high grafting densities
and has been shown to grow well-defined, controllable polymer brush films from many different surfaces.\textsuperscript{64, 89} One downfall of the grafting from technique is that it requires a controlled chain-growth mechanism in order to produce uniform films with controlled thickness. The issue with this requirement is that, to date, well-defined polymer brushes are typically synthesized from vinyl monomers using living polymerization techniques such as cationic polymerization,\textsuperscript{184} anionic polymerization,\textsuperscript{78} living radical polymerization (LRP),\textsuperscript{185} and ring-opening metathesis polymerization (ROMP).\textsuperscript{186} Recently, the vast majority of published brush work has focused on the various LRP techniques, which include reversible addition-fragmentation chain-transfer (RAFT) polymerization,\textsuperscript{58} atom transfer radical polymerization (ATRP),\textsuperscript{187} and nitroxide mediated polymerization (NMP);\textsuperscript{188} and they have encompassed a wide range of topics that include block copolymer brushes and brushes with stimuli responsive behavior.\textsuperscript{95, 99, 102, 189-191}

The structure of brushes prepared from vinyl monomers is believed to be a compressed random coil that is extended normal to the surface.\textsuperscript{8, 97} While the compressed random coil structure of polymer brushes induce many interesting surface effects, the ability to prepare polymer brushes with chains that are more or completely extended relative to the surface and tightly-packed relative to each other would open an interesting and new field of research. The high degree of alignment and intermolecular forces that would be present it such systems, could be utilized in a wide range of applications that require high degrees of ordering such as increased charge mobility, improved strength, and impressive thermal integrity that would improve upon the current random coil brushes.

Rigid rod polymers typically obtain their rigidity from monomers that have aromatic character within the backbone, along with bonding that exhibits restricted bond rotation and often results in polyaromatic systems. Conventionally, rigid rod aromatic polymers are synthesized via a step-growth mechanism, however, this mechanism cannot produce well-defined polymer brushes via the grafting from technique due to the monomer self-condensing polymerization mechanism in solution and the subsequent attachment of the oligomers on the surface. As such, in order to
prepare well-defined polymer brushes resembling these impressive materials, a living chain-growth mechanism is required.

The chain growth condensation (CGC) polymerization technique was originally demonstrated by Yokozawa in 2000 and has since been reviewed extensively. The first way mentioned to utilize the chain growth condensation mechanism is to use substituent effects to deactivate A-B monomers’ reactivity towards one another, while also introducing a highly reactive activated initiator, such that the monomer preferentially reacts with that initiator, allowing for growth from the end of the chain. This method has been used for the preparation of well-defined polyamide analogs with soluble aliphatic side chains, controllable molecular weights, and narrow molecular weight distributions. The other CGC mechanism utilizes a transition metal catalyst ring walking method. This is where it is believed that the monomer adds to the bound catalyst at the end of the chain, the catalyst is then believed to “walk” across the new monomer and reinserts itself at the end of the chain and the process repeats itself. Despite the tremendous interest in CGC polymerization, its use in the preparation of polymer brushes has been limited to metal catalyst-based systems and, to the best of our knowledge, has never been reported for the preparation of aramid brushes.

Due to their importance in a wide variety of applications, aramids, specifically when spun into fibers, have been studied extensively for high-strength and high-temperature applications. The impressive properties of these materials stem from the rigid aromatic behavior of the polymer backbone, along with the hydrogen bonding between the amide linkages of different chains, and the high degree of ordering of the elongated chains along the length of the fibers, which imparts strength and resistance to thermal degradation. Aramids have a wide variety of applications outside their use in fibers, including use in aerospace applications, fuel cell membranes, and as antifouling agents in reverse osmosis membranes. Each of these applications takes advantage of the aramid to introduce new and beneficial surface properties but suffer from harsh coating conditions, coating instabilities, and difficulty in producing well-defined controllable films.
The development of aramid brushes has the potential to overcome these issues, improve the properties of the aramid coatings in these systems, and also introduce these unique polymer films to other applications.

Recently, there has been some interest in producing surface-bound aramids using sequential molecular layer deposition of A-A and B-B monomers. Very thin oligomer amide films were successfully grown from high surface area silica and monitored by in-situ Fourier transform infrared (FTIR) spectroscopy using molecular layer deposition (MLD). Polyamide films of Nylon 6,6\textsuperscript{174} and poly(p-phenylene terephthalamide)\textsuperscript{175} were grown by performing sequential, self-limiting surface reactions between the diacid chloride and diamine of the respective monomers. However, even though this technique creates the desired aramid thin film directly from a surface, the technique is cumbersome, due to the arduous reaction conditions necessary, such as high vacuum and high temperature. The method also produces disordered films that are not well-controlled and limited to the addition of a small number of monomers. The MLD method also tends to be very time consuming due to the nature of introducing sequential monomer gasses that undergo self-limiting gaseous surface reactions. It would be very beneficial to be able to produce controllable and desirable aramid films at lower temperatures via solution processable conditions.

In this chapter, we have modified a previously reported CGC polymerization procedure for the preparation of aramids,\textsuperscript{192} to synthesize the first examples of aramid brushes via a CGC grafting from technique. To achieve this, a highly activated ester-amide terephthalate initiator was designed and synthesized with the ability to attach to well-defined silica surfaces. Aramid brushes were grown from surface immobilized initiators in a controlled manner via CGC of the monomer, methyl 4-(octylamino)benzoate, to produce surface-grafted rigid rod aramids. The aramid brushes were grown from both flat silicon wafers and high surface area silica nanoparticles. In each case, well-defined polymer brushes with controllable thickness and high grafting density were produced. With an improved understanding of this new CGC brush technique, these results can be utilized to design and develop new surface initiated polymer brushes that utilize the CGC technique.
3.2 Experimental Section

3.2.1 Materials

Lithium 1,1,1,3,3,3-hexamethyldisilazide (LHMDS, 1.0 M) in tetrahydrofuran (THF), dimethylamine solution (2 M, THF), triethylamine (>99.5%), thionyl chloride (SOCl₂, >99.5%), anhydrous dichloromethane (DCM) (stabilized with 50-150 ppm amylene, >99.8%), octanal (99%), sodium triacetoxyborohydride (97%), tetraethylorthosilicate (TEOS, 98%), and MgSO₄ were purchased from Sigma-Aldrich. Dichloromethane (DCM), acetic acid, NaHCO₃, aqueous H₂O₂ (30%), pentane, and ethyl acetate were purchased from Macron. N-methylaminopropyltrimethoxysilane was purchased from Gelest, 4-(methoxycarbonyl)benzoic acid from Matrix Scientific, ethanol (200 proof, absolute) from Pharmco-AAPER, aqueous ammonia (28-30%) from Mallinckrodt Baker, ammonium chloride (99.9%) from Baker Scientific, methyl 4-aminobenzoate (98%) from Alfa Aesar, H₂SO₄ (95.0-98.0%) from EMD Performance Materials, and aqueous hydrofluoric acid (HF) (49%) from Fisher Scientific. Unless otherwise mentioned, all chemicals were used as received without further purification. THF and toluene solvents were purchased from Macron and were purified and dispensed through a PURE SOLV MD-4 solvent purification system (activated alumina, copper catalysts, and molecular sieves). Silicon wafers (prime grade, single side polished) were obtained from Wafer World, with only a native oxide.

3.2.2 Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on a JEOL-500 S MHz spectrometer. Bulk infrared spectra were recorded on a Thermo Scientific Nicolet iS50 FTIR spectrometer using a diamond attenuated total reflectance (ATR) crystal for bulk samples, while thin films on silicon wafers were measured using a Harrick Scientific VariGATR accessory (grazing-angle ATR (GATR)). Ellipsometric measurements were carried out on a VB-250 VASE series ellipsometer, with a HS-190 monochromator and a 70 degree angle of incidence. Refractive indices were fixed at 1.45 for all respective surface modifications and brushes and a thin film of
silica on silicon model was used to calculate thicknesses. Contact angle measurements were recorded using a ramé-hart Standard Goniometer 200-00 using 10 µL drops of deionized ultrafiltered (DIUF) water. Images were processed using DROPImage Software. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 using air at a flowrate of 30 mL/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electron 5800 ultra-high vacuum XPS-Auger spectrometer at Colorado State University. The incidence angle of X-ray was 45° with respect to the surface normal. Number average molecular weight (M<sub>n</sub>) and polydispersity index (M<sub>w</sub>/M<sub>n</sub>, PDI) were measured using a Viscotek GPCmax gel-permeation chromatography (GPC) unit (eluent: stabilized tetrahydrofuran (OmniSolv) with a flow rate of 1.0 mL/min using PLgel 5µm MIXED-C and MIXED-D columns: molecular weight range 200-2,000,000 and 200-400,000g/mol (polystyrene equivalent), respectively). A calculated dn/dc value of 0.156 was determined and used during the analysis. Stöber particles were characterized and sizes were measured using a JEOL JSM-7000F scanning electron microscope (SEM) with a Schottky cathode field emitter at 20kV. Samples were sputtered with gold to make conductive.

3.2.3 Synthesis Methods

3.2.3.1 Synthesis of Monomer and Initiators

Methyl 4-(Octylamino)benzoate (2)

The procedure used to prepare the methyl 4-(octylamino)benzoate was adapted from literature. Product: as white crystals: m.p. 90-91 °C [literature m.p. 86.5-87.3],<sup>192</sup> (8.5 g, yield: 71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, J = 8.9 Hz, 2H), 6.53 (d, J = 8.9 Hz, 2H), 4.13 (br, 1H), 3.83 (s, 3H), 3.14 (t, J = 7.2 Hz, 2H), 1.62 (quint, J = 7.4, 2H) 1.42-1.22 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.23, 29.16, 29.1, 27.0, 22.5, 14.0. FTIR (ATR) 3375, (Ar-NH-R), 2946, 2920, 2848, 1678 (-CO-O-), 1596 cm<sup>-1</sup>.
Methyl 4-(Dimethylcarbamoyl)benzoate (DMA, (1))

A solution of dimethylamine (4 mL, 8 mmol), triethylamine (0.87 mL, 6.3 mmol) and anhydrous DCM (15 mL) was prepared and added to a solution of the acid chloride (methyl 4-(chlorocarbonyl)benzoate) (1.13 g, 5.7 mmol) (prepared by refluxing 4-(methoxycarbonyl)benzoic acid (1.03 g, 5.7 mmol) in SOCl$_2$ for 2 h, and removing excess SOCl$_2$) in anhydrous DCM (5 mL). The solution was refluxed for 1 h followed by concentration in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel (pentane/ethyl acetate 1:1) yielding product as fine, pale-yellow crystals: m. p. 108-109 °C, (1.1 g, yield: 91%). $^1$H NMR (500 MHz, CDCl$_3$, 25°C): $\delta$ = 8.06 (d, $J = 8.32$ Hz, 2H), 7.47 (d, $J = 8.32$ Hz, 2H), 3.92 (s, 1H), 3.11 (br, 3H), 2.94 (br, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) 170.5, 166.5, 140.7, 131.0, 129.7, 127.2, 52.4, 39.4, 35.3 ppm; FTIR (ATR): 2951, 2853, 1721, 1618, 1277, 1257, 1109, 1078, 726 cm$^{-1}$.

Methyl 4-(Methyl(3-(Trimethoxysilyl)propyl)carbamoyl)benzoate (TMS-Amide, (3))

A similar procedure to that reported in literature$^{196}$ was used with N-methyl-3-(trimethoxysilyl)propan-1-amine used in place of the 3-(triethoxysilyl)propan-1-amine. Briefly, a solution of N-methyl-3-(trimethoxysilyl)propan-1-amine (1.0 g, 5.18 mmol) and triethylamine (0.73 g, 7.25 mmol) in anhydrous DCM (20 mL) was added to a solution of the acid chloride (methyl 4-(chlorocarbonyl)benzoate) (1.1 g, 5.55 mmol) in anhydrous DCM (20 mL). The solution was refluxed for 1.5 h followed by concentration in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel (pentane/ethyl acetate 1:1) yielding the trialkoxysilane as a pale yellow oil (1.2 g, yield: 66%). $^1$H NMR (500 MHz, CDCl$_3$, 25°C): $\delta$ = 8.05 (d, $J = 8.19$ Hz, 2H), 7.42 (d, $J = 8.05$ Hz, 2H), 3.91 (s, 1H), 3.57, 3.49 (2s, 9H), 3.51, 3.15 (2t, $J = 7.36$ Hz, 2H), 3.05, 2.88 (2s, 3H), 1.77, 1.61 (2m, $J = 7.05$, 2H), 0.68, 0.37 (2t, $J = 8.02$, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) 170.6, 170.0, 166.0, 141.0, 130.6, 130.5, 129.5, 129.4, 126.7, 126.5, 53.2, 52.0, 50.2, 49.6, 37.0, 32.3, 21.2, 19.9, 6.18, 5.65 ppm; FTIR (ATR): 2942.4, 2840.1, 1721.2, 1632.7, 1434.7, 1401.4, 1274.1, 1189.5, 1069.6, 813.3, 785.1, 733.5 cm$^{-1}$.
3.2.3.2 Polymerization Methods

Deposition of TMS-Amide Initiator on Silicon Wafers Surface (4)

Fresh cut silicon wafers were cleaned with freshly made piranha solution (30:70 30% H₂O₂:conc. H₂SO₄) at 100 °C for 2 h. Caution: piranha solution is extremely caustic and should be handled with care. The wafers were removed and washed 3 times with DIUF water and dried under filtered air. The wafers were then placed directly into 10 mL reaction flasks. Anhydrous toluene (10 mL) and TMS-Amide (70 mg, 0.2 mmol) were placed in the flask and was capped with a glass stopper. The solution was heated to 100 °C for 2 h. The wafers were then removed, washed twice with fresh toluene and dried under filtered air. The wafers were then annealed in a 120°C oven (air) for 30 min to remove any condensation products.

Preparation of 500 nm Stöber Silica for High Surface Area Samples

Stöber particles, approximately 500 nm in diameter, were synthesized by adding 300 mL of absolute ethanol and aqueous ammonia (100 mL, 1.45 mol) into a 500 mL round bottom flask with a stir bar. TEOS (25 mL, 112 mmol) was added at room temperature while stirring vigorously. After 12 h, the particles were washed four times with anhydrous ethanol using sonication/centrifugation wash cycles. The particles were then dried in a vacuum oven, calcined in tube furnace at 600 °C for 12 h, re-dispersed in DIUF water and freeze dried to a fine white powder. Particles were characterized using SEM.

Deposition of TMS-Amide Initiator on Stöber Silica Surface (4)

6 g of calcined Stöber Silica was placed directly into a 500 mL round bottom reaction flask. Anhydrous toluene (350 mL) and TMS-Amide (1.67 g, 4.71 mmol) was added to the flask, which was then capped with a glass stopper. The solution was heated to 100 °C for 2 h with stirring. The particles were then washed with repeated centrifugation/suspension twice in toluene and once in THF using glass centrifuge tubes. The resulting powder was dried in a vacuum oven to give an off-white powder.
**Formation of Polymer Brushes on Silicon Wafer Surface**

TMS-Amide-modified wafers were placed into a 10 mL reaction vessel along with a stir-bar, monomer (2) (0.13 g, 0.5 mmol) and capped with a septum. The flask was purged with argon for 10 min and filled with degassed, anhydrous THF (10 mL). The reaction was placed in an ice bath and allowed to cool for 10 min at 0 °C. LHDMS (0.5 mmol, 0.5 mL) was then added to deprotonate the monomer and start the polymerization from the surface. The reaction was allowed to proceed for a desired time (0-12 h) and the wafers were then removed, washed with DCM, THF and DIUF water and dried under filtered air. The wafers were finally annealed in an oven (120°C) for 30 min before characterization.

**Formation of Polymer Brushes on Stöber Silica Surface**

TMS-amide modified Stöber silica (1 g) was placed into a 100 mL Schlenk flask reaction vessel along with a stir-bar, monomer (2) (0.26 g, 1 mmol) and capped with a septum. The flask was purged with argon for 10 min and then degassed, anhydrous THF (10 mL) was added. The reaction was placed in an ice bath and allowed to cool for 10 min at 0 °C. LHDMS (1.0 mmol, 1.0 mL) was added to deprotonate the monomer and start the surface polymerization on the silica. The reaction was allowed to proceed for a desired time (0-12 h) and quenched with saturated ammonium chloride solution. The polymer-coated Stöber silica was isolated by repeated centrifugations and washings with DIUF, DCM, and THF using glass centrifuge tubes and sonication. The organosilica particles were then dried in vacuum oven (120 °C) for 1 hour before characterization.

**Digestion of Stöber Silica Using Aqueous HF**

Polymer-coated silica particles (~1 g) were placed into 10 mL polypropylene vials with 5 mL of DIUF water and 2 drops of 49% aqueous HF and stirred overnight. The polymer was liberated after digestion of the silica particles and floated to form an insoluble cluster. The polymer was extracted with DCM, separated from the aqueous layer and dried in vacuo.
3.3 Results and Discussion

In order to prepare well-defined polymer brushes, a living chain-growth polymerization technique is required to effectively graft from surfaces. A wide variety of polymerization techniques have been demonstrated to achieve this, but they typically limit the polymers to those prepared from conventional vinyl monomers. To date, LRP techniques have dominated the polymer brush literature and they have demonstrated very interesting polymer brush architectures, functionality, and applications; however, these structures are primarily limited to compressed random coil polymers. In order to expand the potential applications of polymer brushes, it is imperative to be able to prepare brushes with new functionalities and structures. In the search for new polymer brush structures, it would be very beneficial to be able to grow brushes of polyaromatic macromolecules, due to their impressive properties that stem from the rigid character of their aromatic backbone and intramolecular forces. Typically, polymers with aromatic backbones are prepared using step-growth polymerization, a process that is not suitable for preparing well-defined polymer brushes.

Previously, polyamide brushes were attempted using the step-growth techniques and controlling the growth using MLD for Nylon 6,6 and poly(p-phenylene terephthalamide), however, these methods used complicated reactions between gases and the surface under high vacuum, control over polymer growth was not maintained, and the average degree of polymerization was very low.

These issues with producing aramid brushes can be addressed by utilizing a fairly new polymerization technique: CGC via substituent effects. It was recently demonstrated that conventional step-growth polycondensation techniques can be converted to chain-growth by using either substituent effects or catalyst ring walking techniques, and, therefore, potentially allows for the preparation of brushes from these interesting methods. Despite this, to date, only the metal catalyst walking method has been used to prepare polymer brushes. To the best of our
knowledge, the preparation of aramid brushes have not been demonstrated using a surface-initiated, chain-growth mechanism in solution and our results are reported herein.

3.3.1 Design of Functional Initiator and Solution Polymerizations

In order to design an initiator that exhibits 1) activated character with respect to substituent effect CGC, and 2) is able to attach to silica surfaces, a model initiator that would mimic a surface attached moiety was synthesized and tested to probe its effectiveness in growing well-defined aramids. An ester/amide terephthalate moiety was chosen as a potential candidate, due to its more activating electron-withdrawing para carbonyl functionality, which should improve the initiation efficiency of the system and also allow for para attachment to various grafting functionalities via the amide bond. To achieve this, the designed initiator should have a terminal methyl ester (mimicking the growing polymer chain) and a secondary amine attached to a terminal trimethoxysilane, which can later be tethered to a surface. As such, a dimethylamide terminated initiator (1) was synthesized to investigate the effectiveness of a model initiator in solution. NMR and FTIR results demonstrate that (1) could be prepared in both high purity and high yield. To test the initiation effectiveness of (1) for CGC, polymerizations of the deactivated monomer methyl 4-(octylamino)benzoate (2) with (1) as the initiator were conducted using literature conditions at 0 °C (Scheme 3.1).

Scheme 3.1. Solution polymerization of (2) to test the effectiveness of a model initiator (1).
During the course of the polymerization samples were removed, quenched into aqueous saturated ammonium chloride, extracted with DCM, dried, and analyzed using NMR spectroscopy. The conversion was monitored by examining the relative ratios between the monomer aromatic doublets at 8 and 6.5 ppm and the polymer aromatic signals at 7.5 and 7 ppm. Using these ratios, the controlled nature of the CGC reaction was investigated (Figure 3.1). The semilogarithmic plot of conversion versus time (Figure 3.1a) shows a linear correlation of monomer conversion with time, which is consistent with a controlled polymerization with first order kinetics. The rate constant for the CGC reaction was derived from the slope of the semilogarithmic plot and was determined to be $0.04 \text{ M}^{-1}\text{s}^{-1}$. The same kinetics samples were used to plot $M_n$ versus conversion (Figure 3.1b), which demonstrates a linear correlation where the experimental molecular weights closely match the theoretical values. Next the effectiveness of our initiator and the controlled nature of the polymerization was investigated by using different feed ratios of (2) to (1) and the results were similar to literature. Four polymerizations took place with different feed ratios of (2):(1), ranging from 10:1 to 40:1, and were allowed to go to 100% conversion (Figure 3.1c). The $M_n$ of the polymers was measured using NMR and GPC to compare the experimental and theoretical $M_n$ values and also to determine the PDI of the polymers. Results from this study demonstrate that the experimental $M_n$ values, determined by NMR, closely match the theoretical $M_n$ values. However, the GPC results provide $M_n$ values that are slightly lower than theoretical because the calculations are based off of polystyrene standards. The GPC results also show that the PDI’s of the polymers obtained at different feed ratios were all less than 1.1, suggesting fast initiation and a well-controlled CGC polymerization (Figure 3.1d). The combination of all of these results demonstrate that the newly designed initiator, (1), exhibited a quick initiation relative to propagation, even with the terminal methyl ester in place of the phenyl ester used in literature, and produced polymer with living chain growth characteristics and controllable molecular weights with predetermined feed ratios of (2) to (1).
Figure 3.1. (a) Semilogrithmic plot, (b) the correlation between $M_n$ and conversion from kinetics samples, (c) $M_n$ values resulting from different initial feed ratio of (2):(1) after 100% conversion calculated from NMR and GPC, and (d) $M_w/M_n$ calculated from GPC of samples in (c) all demonstrating the well-controlled CGC polymerization.

### 3.3.2 Synthesis of Silane Based CGC Initiator (TMS-Amide)

Based on the successful results obtained for the model dimethylamide terminated initiator (1) in solution, a surface graftable silane based initiator, TMS-Amide (3), was synthesized by reacting a secondary amine bearing a trimethoxysilane with monomethyl ester terephthalate acid chloride (Scheme 3.2a). After purification using column chromatography, (3) was obtained at moderate yields and the structure was confirmed by NMR and FTIR. The initiator was designed with a silane anchoring group, to enable attachment to silica surfaces, in addition to the activating electron-withdrawing para carbonyl functionality to make it an efficient initiator in CGC.
3.3.3 Deposition of TMS-Amide on to SiO$_2$/Si Wafers

The previously prepared initiator for surface-based CGC was deposited on piranha-cleaned silicon wafers in hot anhydrous toluene, rinsed with fresh toluene, dried, and annealed to remove the condensation products and secure the initiator layer to the wafer (Scheme 3.2b). The deposited initiator was characterized using goniometry, ellipsometry, FTIR spectroscopy, and XPS. Goniometry results from the wafers before and after surface modification showed an increase from a surface that is essentially completely wetted (~1-3°) for clean wafers to a contact angle of 53±3° for the wafers with the deposited TMS-Amide initiator. These results are consistent with a change from the initial hydroxylated silicon surface to the more hydrophobic aromatic methyl ester. Ellipsometry measurements show that the thickness of the film increases from the initial silica layer thickness of 1.5±0.1 nm to a thickness 2.9±0.1 nm, using the same SiO$_2$ model to fit the data, after deposition of the initiator. The 1.4 nm TMS-Amide film is very close to the 1.39 nm calculated film thickness of a monolayer of TMS-Amide molecules that are perpendicular to the surface, also suggesting very little crosslinking and aggregation of the silane molecules on the surface. The small error in the measurements also demonstrates a good model fit to the ellipsometry data, also suggesting a relatively uniform TMS-Amide film.
GATR-FTIR performed on the deposited TMS-Amide film on silicon wafers showed good spectral overlap between the modified surface and ATR-FTIR of the neat TMS-Amide (Figure 3.2). Pertinent absorption bands indicative of the TMS-Amide molecule are evident with peaks at approximately 2850 and 2930 cm\(^{-1}\), which correspond to the CH\(_2\) stretching and C-H vibrations, respectively, along with peaks at 1730 cm\(^{-1}\), pertaining to the ester stretch, and 1650 cm\(^{-1}\), corresponding to the amide carbonyl stretch. The peaks not matching the neat TMS-Amide spectrum at 1200 cm\(^{-1}\) and 900-800 cm\(^{-1}\) are present in a spectrum for clean, unmodified silicon wafers and can be assigned to the Si-O-Si stretch and Si-O-H stretch & bend modes for silica, respectively.\(^{198}\) The peak at 1100 cm\(^{-1}\) is a peak that shows up after the silane deposition and can be assigned to chemisorbed Si-O-Si from the TMS-amide.\(^{198}\)

![ATR-FTIR Spectra](image)

**Figure 3.2.** ATR-FTIR spectra of neat TMS-Amide (3) overlaid with a spectra of the deposited TMS-Amide film (4) using GATR-FTIR spectroscopy.
XPS analysis of the deposited TMS-Amide film showed all of the expected elements: carbon, nitrogen, oxygen and silicon (from the substrate). Both survey and high resolution (HiRES) values were included, along with adjusted atomic ratios, which were calculated by removing the silicon and the two oxygens for every silicon that exists in the oxide layer using the obtained ratio of Si in SiO$_2$/Si metal, which was 32% (Table 3.1). The adjusted values for the TMS-Amide layer are within 8%, which could be a product of the assumption made when calculating the theoretical values (no silicon), the actual attachment chemistry (regarding how many unreacted methoxy groups are present), and the amount of adventitious carbon present on the sample. The XPS survey scans from TMS-Amide modified surface (Figure 3.3a) is indicative of a very thin silane film, due to the presence of the respective atoms and the relatively high silicon and oxygen signal penetrating from the native silica layer below. The combination of the ellipsometry, contact angle, GATR, and XPS results suggests that the TMS-Amide CGC initiator was successfully deposited on the SiO$_2$/Si wafers.

Figure 3.3. Wide-scan X-ray photoelectron spectra of (a) TMS-Amide initiator deposition and (b) aramid brush grown using surface-initiated CGC polymerization technique.
Table 3.1. Collected and adjusted\textsuperscript{a} atomic percentages of modified silicon surfaces from wide-scan and high-resolution X-ray photoelectron spectroscopy.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wide-Scan</th>
<th>HiRES</th>
<th>Adjusted</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
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<td>29.0</td>
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<td>76.5</td>
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<tr>
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<td>0</td>
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<tr>
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<td>3.4</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
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<th>HiRES</th>
<th>Adjusted</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
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<td>84.5</td>
<td>88.9</td>
<td>88.2</td>
</tr>
<tr>
<td>O 1s</td>
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<td>7.4</td>
<td>5.7</td>
<td>5.9</td>
</tr>
<tr>
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<td>0</td>
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<tr>
<td>N 1s</td>
<td>5.0</td>
<td>5.1</td>
<td>5.4</td>
<td>5.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Atomic percentages were adjusted by removing the expected percentages of oxygen that would exist from the native oxide. The ratio of SiO\textsubscript{2} Si/Metal Si was 32%.

3.3.4 Growth of Aramid Brushes using CGC from Surface-Immobilized Initiators on Flat Silicon Substrates.

To determine the effectiveness of the surface immobilized TMS-Amide initiator for CGC, aramid brushes were grown by immersing the initiator-modified silica wafers in a solution of deprotonated monomer in THF at 0 °C (Scheme 3.3). After the polymerization, the modified wafers were extensively cleaned via sequential solvent treatment to remove excess monomer and ensure characterization was focused on the surface immobilized polymer. The successful formation of surface initiated polymer chains was confirmed using goniometry, ellipsometry, FTIR spectroscopy, and XPS. Goniometry measurements demonstrated that the contact angle of the wafer increased from 53±3° to 78±3° after polymerization, suggesting a more hydrophobic surface.
indicative of the alkyl solubilizing groups in (2) that would be incorporated on the surface as part of the repeating unit of the polymer chain. The contact angle measurements for the brush film is comparable to results for a spin-coated film of poly(2), 80±2°. GATR-FTIR measurements (Figure 3.4) also indicate that the surface-immobilized polymers had near perfect spectral overlap to that of polymer prepared in solution using the CGC. The pertinent peaks are the C-H stretches and bends near 2850 and 2930 cm⁻¹, along with the small signal at 1730 cm⁻¹ indicative of the ester end group, and the large amide stretch at 1650 cm⁻¹, corresponding to the more common amide linkages found along the polymer backbone.

Scheme 3.3. Surface initiated poly(2) brushes from surface bound TMS-Amide initiators (4).

Ellipsometry was used to study how the film thickness changed with time and see if the polymerization is controlled from the surface by observing a linear growth with time and, hence, conversion. Initiator-modified wafers were placed in the monomer solution for a designated amount of time and were then removed, cleaned and the thickness was measured. The ellipsometry results shows that the thickness of the aramid brushes increase linearly with reaction time, suggesting controlled polymer growth (Figure 3.5). The same wafers were then measured using GATR-FTIR to examine the correlation between the growth of the polymer brush and the observed peak intensities (Figures 3.5 & 3.6). These results demonstrated a notable increase in the aliphatic C-H signal intensity (near 2850 and 2930 cm⁻¹) with time, which is consistent with
the increasing amount of aliphatic sidechains intrinsic to increasing molecular weights. The amide intensity (at 1650 cm\(^{-1}\)) also increases with time, which is expected with increasing molecular weight, due to the increasing number of amide bonds linking the monomers together. It can also be observed that the ester stretch intensity (at 1730 cm\(^{-1}\)) remains constant throughout the kinetics experiments, which is expected since the ester end group of the polymer would remain at a constant concentration throughout the polymerization. Therefore, when both of the ellipsometry and GATR trends were plotted together vs. time, an interesting correlation between brush thickness and amide stretch intensity from GATR was apparent (Figure 3.5).

To provide further evidence of aramid brush formation, XPS was performed on the polymer brush films (Table 3.1). The atomic percentages collected from the wide-scan and high-resolution data agree well and, once adjusted for the oxygen that corresponds to the oxygen in the native

![Graph showing FTIR spectra comparison](image)

Figure 3.4. Comparison between the FTIR spectra of polymer grown in solution and the thin film aramid brush on silicon wafers.
Figure 3.5. A correlation between film thickness using ellipsometry and amide peak absorbance (at 1650 cm\(^{-1}\)) from GATR-FTIR spectroscopy as a function of polymerization time.

Figure 3.6. GATR-FTIR spectra of aramid brush growth with time using surface initiated CGC polymerization technique.

silicon oxide, closely match the theoretical percentages. The survey scan in Figure 3.3b shows an increase in the nitrogen and carbon signals, with a larger inelastic scattering rise from carbon. There is also a decrease in the oxygen signal, with very little-to no silicon signal, suggesting a
thicker polymer film (>10 nm) with good coverage over the surface and little indication of the presence of the underlying silica film.

3.3.5 Living Character of the Aramid Brushes

One of the primary advantages of using living chain growth polymerization mechanisms in the preparation of polymer brushes is the ability to reinitiate the polymer chains to continue the polymerization, or produce block copolymer brushes. However, with the use of conventional living polymerization techniques, such as LRP, for the preparation of polymer brushes, there is always a possibility of termination or chain transfer reactions occurring, both of which will have a large impact on the properties and structure of the resulting brush. The CGC technique, as mentioned previously, is a very different polymerization technique than LRP. There are no radicals, so therefore all radical termination and chain transfer mechanisms do not apply. CGC systems have end groups that are more inert to the polymerization environment and remain active as long as no inert end group is introduced intentionally to stop the reaction. Because there are no termination mechanisms by virtue for these systems, it is envisioned that large molecular weights can be achieved as long as the polymer remains soluble with an end group available for reaction. This is potentially beneficial when designing new polymer brush systems, because well-controlled brush films can be achieved.

Even though high molecular weights are envisioned for these systems, it is reported, in solution, that at high molecular weights (feed ratios > 75) the molecular weight distributions became broader and controlled growth is lost due to step-growth behavior dominating the polymerization.\textsuperscript{192} We propose that this is actually potentially due to the loss of solubility of the growing polymer chains due to the insoluble by-products of the condensation.

It was observed that, even though brushes prepared using CGC should have no termination mechanism, the aramid brushes prepared in this study would grow to a certain thickness and stop, even after prolonged polymerization times (<12 h). It was also observed that after wafers were removed from the solution, when the polymer brush thickness had stopped growing, and
rinsed with THF, a visible film appeared to coat the surface. Since no free initiator was added to the systems, no free polymer was formed in the polymerization solution, and the monomer is completely soluble in the solvent used as such, this film was believed to come from some other component in the system. In addition, organic solvents such as THF, DCM, chloroform, and hexane would not remove this film, but polar-protic solvents, such as methanol and water, rapidly dissolved the film, exposing the optically smooth brush surface. Based on these observations, we hypothesize that the observed film is caused by the insoluble lithium methoxide salt that is liberated every time monomer is added to the growing chain. To test this hypothesis, lithium methoxide salt was formed in THF (the solvent used for the polymerization) by adding 40 µL (1 mmol) of methanol to 10 mL of anhydrous THF, followed by the addition of 1 mmol (1 mL) of 1 M LHMDS in THF. In this experiment, as soon as the LHMDS was added to the solution, it turned cloudy, which confirms that the deprotonated methanol forms an insoluble lithium methoxide salt in THF. In addition, there have been previous reports that investigated the solubility of lithium methoxide in lithium ion batteries, where the lithium methoxides solubility in different solvents, similar to but not including THF, were calculated. These results demonstrated that the small molecular nature and tight packing in the crystal structure of lithium methoxide gave exothermic heats of dissolution in dimethylcarbonate and ethylene carbonate, which are both more polar than THF and suggests that THF is not a good solvent for lithium methoxide salts.199

We find that the aramid brush results agree with the solution polymerization observations. It was observed that throughout the course of a solution polymerization, the solution became more cloudy with time, presumably due to continued formation of lithium methoxide as monomer is added to the polymer chain. When the polymerization was completed and quenched with aqueous ammonium chloride, the solution became clear, signifying the protonation and dissolution of the methoxide, returning the ‘salt’ back to solution.

To confirm that blocking of the reactive polymer end groups was responsible for halted growth of the polymer brushes and not termination or side reactions, the wafers were removed from the
solution, cleaned using methanol, water, and organic solvents, characterized, and reinserted to a new monomer solution in an attempt to reinitiate the polymerization. These results demonstrated that indeed, after removal of the film on the surface of the polymer brush, chain extension does occur as the thickness of the polymer brushed increased, as determined by ellipsometry and GATR-FTIR spectroscopy (Figure 3.7). This experiment was conducted by first performing a polymerization from the surface (< 12 h) followed by characterization as mentioned above. The same characterized wafer was used to perform another polymerization using the same previous procedure. The brush saw an extension via ellipsometry from 9 nm to a new thickness of 12 nm. However, only a 3 nm increase was observed after the same reaction time, indicating that the brush did not grow to the same extent. It is possible that the solvent washing procedures only removed the surface layer of lithium methoxide, leaving embedded salt that would interfere with the chain extension procedure.

We are currently studying how to resolve this ‘termination’ issue by utilizing solubilizing crown ethers, different cations, and more soluble leaving groups, such as lithium ethoxides or phenoxides for example, and is a topic for an upcoming paper.

![Figure 3.7. Evidence of brush reinitiation and chain extension using GATR FTIR.](image)

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3.3.6 Growth of Aramid Brushes using CGC from Surface-Immobilized Initiators on High Surface Area Silica

In order to gain more information on the surface-initiated aramid brushes, brushes were also grown from silica nanoparticles that had been modified with the TMS-Amide initiator (Scheme 3.4). The use of a high surface area substrate, such as the silica nanoparticles, allows for a better understanding of the grafting density, kinetics, and molecular weight properties of the formed polymer brushes, since a quantitative amount of polymer can be recovered after digestion of the silica spheres using aqueous HF. Relatively large diameter Stöber silica nanoparticles (~500 nm) were synthesized, calcined, rehydrated, and freeze dried to mimic depositions on flat silicon wafers. The surface initiator was deposited on the Stöber silica by stirring the particles in hot anhydrous toluene with the TMS-Amide initiator. Brushes were grown from the cleaned and dried initiator-modified particles by placing them in a flask with the monomer, THF and base to start the reaction from the surface (Scheme 3.4). After extensive washings and centrifugations, the particles were dried and characterized.

![Scheme 3.4. Deposition of TMS-Amide initiator (3) on silica nanospheres along with polymer growth from surface modified Stöber silica nanoparticles using CGC polymerization. Surface diagrams and curvature not to scale.](image-url)
To demonstrate the successful formation of the aramid brushes, FTIR spectra were taken of the coated nanoparticles, using ATR, and showed signals that closely match the characteristic aliphatic and carbonyl stretches of free polymer (ATR) and the flat surface brush (GATR). This data can be found in the Appendix A. In addition, the calcined silica particles, particles modified with the TMS-Amide initiator, and the particles after a representative surface-initiated CGC polymerization were all analyzed using TGA (Figure 3.8). From the TGA traces, it is apparent that the calcined particles lost very little mass (< 0.25 wt.%) up to 700°C, indicating successful calcination and that the spheres are essentially only SiO$_2$. The TGA trace for particles coated with TMS-Amide initiator lost approximately 1 wt.% of mass, which corresponds to approximately 5 initiator molecules/nm$^2$ on the surface of the silica particles. This calculation was performed by converting the wt.% lost to a mass using the original mass of particles, converting this mass to a number of molecules using the burnable portion molar mass of the surface immobilized initiator (234 g/mol) and dividing the number by the surface area of the 500 nm spherical particles (4.53x10$^{18}$ nm$^2$/g).

TGA was performed on the polymer brush particles as well and the decomposition profile became more pronounced and exhibited a distinct bimodal decomposition that mimics the TGA profile of free polymer (seen in Appendix A). Polymer grafting densities were calculated using the same procedure by examining TGA burnoff and using the $M_n$ of the detached polymer, determined from digestion of the particles, which will be described in further detail later. A constant brush grafting density of 0.35 chains/nm$^2$ was obtained for all samples, which is ~10 times smaller than the initiator layer and is expected due to the steric imposed by the bulky backbone and solubilizing groups.

The thickness of the polymer film on the silica particles was attempted to be monitored using scanning electron microscopy, however, no noticeable changes in thickness was apparent within the resolution of the instrument (~10 nm). The particles did however retain a very smooth surface after both deposition of the initiation and the polymerization.
Figure 3.8. TGA traces of calcined silica particles, particles modified with the TMS-Amide initiator, and the particles after a representative CGC polymerization.

As mentioned previously, one of the primary advantages of performing surface initiated polymerizations from high surface area particles is the ability to de-graft the polymer from the particles, via digestion of the particles in this case, and collect the liberated polymer for further analysis. As such, a series of polymerizations from silica particles modified with the TMS-Amide initiator were conducted for different times. The bound polymer was subsequently liberated from these silica particles by digestion in a 10% aqueous HF solution overnight. The obtained polymer was then characterized using NMR and GPC to determine the \( M_n \) and PDI.

The \( M_n \) values, determined from NMR and GPC, and the calculated monomer conversion were used to prepare kinetic plots (Figure 3.9) that can be compared to those previously discussed from the solution polymerizations (Figure 3.1). The results from the kinetics experiments for surface initiated CGC from the high surface area silica particles demonstrate a linear correlation between \( M_n \) and conversion (Figure 3.9a) and the \( M_n \) calculated from NMR closely match the theoretical values. In addition, the experiments also exhibited a linear
semilogrithmic plot of conversion versus time, suggesting a controlled growth of the aramid brushes and a constant concentration of growing chains (Figure 3.9b). The rate constant for the surface initiated CGC reaction was determined from the slope of the semilogrithmic plot and gave a value 0.05 M$^{-1}$s$^{-1}$, using a constant grafting density value of 0.35 chains/nm$^2$ to estimate the effective initiator and chain concentration. These results demonstrate that the surface initiated rate constant is within error of the rate constant for the polymerization in solution (0.04 M$^{-1}$s$^{-1}$), which suggests that the surface initiated polymerization and the solution based polymerization are occurring by the same mechanism.

Both NMR and GPC results in Figure 3.9a demonstrate that $M_n$ increases linearly with conversion. The NMR results again follow the theoretical line, while the GPC results appear to be greater. The PDI results do not appear in the figure, however, all are around 1.4. We hypothesize that the larger PDI values (when compared to the solution polymerization) and higher than expected molecular weights could arise from the de-grafting procedure, which could produce siloxane end-coupled polymers, along with unreacted TMS-Amide and various oligomers. Another mechanism contributing to broader distributions would be that the growing chains and insoluble salt could sterically block the uninitiated TMS-Amide or oligomers, resulting in a higher PDI.

![Figure 3.9. Kinetic plots for surface initiated CGC aramid brushes post silica digestion. Correlation between $M_n$ and conversion (a), and the semilogrithmic plot of conversion versus time (b).](image)
It is important to note that this polymerization technique is unique, in that it does not require a polymerization to take place in solution, like with LRP brush methods. However, random coil brush literature produced using LRP techniques also report higher PDI’s from the surface, when compared to solution, but they are considered to be ‘close enough’ to the solution polymers formed during the same growth.\textsuperscript{58,200}

We believe that when the solubility issue is addressed and resolved, higher $M_n$’s and lower PDI’s can be achieved when growing rigid rod polymer brushes, to do the more available surface-confined end groups and no termination mechanisms.

\textbf{3.4 Conclusions}

We have created and demonstrated a novel method to grow surface-initiated chain-growth aramid brushes by developing a new initiator molecule with the capability of attaching to silica surfaces. The initiator is composed of an ester/amide terephthalate, with activating electron-withdrawing para carbonyl functionality, to make it an efficient initiator in CGC, and a trimethoxysilane surface-attachable moiety. Using this new initiator, it was demonstrated that chain-growth aramid brushes can be prepared when the activated initiator-modified surface is exposed to a deactivated monomer solution under strong basic conditions. Following this polymerization technique, living rigid rod aramid brushes were produced on both flat silicon wafers and high-surface area silica particles. Characterization of these polymer brushes provided proof that the aramid brushes produced has similar characteristics and behavior to the same polymer prepared in solution. To the best of our knowledge, this is the first example of aramid brushes prepared by a surface initiated chain-growth polymerization technique. The development of this new brush technique potentially provides opportunities to prepare new and interesting polymer brushes based upon rigid rod polymers.
CHAPTER 4
INVESTIGATION OF THE SUBSTITUENT ESTER LEAVING GROUP EFFECT ON SYNTHESIS OF POLY(N-OCTYL-BENZAMIDE) VIA CHAIN GROWTH POLYCONDENSATION

Modified from the paper submitted to Polymer Chemistry

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4.1 Introduction

Polycondensation techniques have been utilized to create a wide variety of polymers that span many disciplines. Typically, polymers derived using polycondensation techniques utilize the conventional step growth method, where functional groups on both sides of the monomers randomly react with one another to assemble the polymer in a stepwise fashion. This process typically produces relatively low molecular weight polymers with a broad molecular weight distribution (polydispersity index, PDI or $M_w/M_n$, approaching 2.0) as the reaction approaches high monomer conversions. In addition, it is difficult to obtain accurate control over the molecular weight in step growth polymerizations and they do not allow for the preparation of well-defined block copolymers or polymers of more complex architecture. In an attempt to overcome these limitations and expand the use of polymers traditionally made via the step growth process, new polymerization methods have developed to produce conventional condensation polymers via a chain growth mechanism, where the reactivity of the polymer end group can be favoured over other reactions.4, 115

The theory and practice behind converting step growth to chain growth polycondensation was pioneered by Yokozawa and coworkers and has been extensively reviewed.5, 112, 114 Utilization of the chain growth polycondensation processes provides control over properties by achieving planned molecular weights with particular chain end
groups, along with producing polymers with a narrow molecular weight distributions. The chain growth polycondensation process as like other traditional living polymerization techniques allows for synthesis of block copolymers, and most interestingly, the synthesis of surface-initiated polymer brushes of polymers traditionally prepared using step growth polymerization.  

Aromatic polyamides or aramids are selected by industry for their impressive mechanical & thermal properties and notable chemical resistance. Conventionally, the most famous aramids, such as Kevlar® and Nomex®, are synthesized using a step growth process where an aromatic diamine is reacted with a corresponding aromatic diacid chloride, producing very robust materials, due to the strength and stability of the aromatic backbones and the presence of hydrogen bonding. Because of their excellent properties, aramids are produced in high volumes every year. Aramids have the potential for an even wider impact on materials science and engineering if they could be produced using a controlled polymerization technique, that would allow for the production of polymers with a predetermined molecular weights and narrow molecular weight distribution. Controlled polymers allow for improved functionality and solubility, and the ability to create more complex architectures such as block copolymers or covalently attaching the polymers to surfaces to produce well-defined polymer films.

With this in mind, Yokozawa and co-workers have developed multiple synthesis schemes that produce living, chain growth condensation aromatic polyamides. This ground-breaking work demonstrated that polymers traditionally prepared by conventional step growth polycondensation techniques could be converted to a chain growth process and opened up the idea that aramids could be produced in a controlled manner to produce polymers with functionality, structure, and properties that have not been previously realized. The mechanism responsible for the conversion from step growth to chain growth involves deactivating the monomer towards self-condensation, while
activating an initiator, or end group of the polymer, so monomer preferentially adds in a chain growth manner.

Recently, our group addressed the challenge of producing aramid brushes utilizing the chain growth polycondensation technique. This was achieved by designing a highly activated chain growth condensation (CGC) initiator that has the capability to attach to silica surfaces. After attachment of the initiator, it was demonstrated for the first time that aramid brushes could be grown from these surfaces using this CGC technique. However, during this study it was observed that while the polymerization would occur as expected, only low molecular weight polymers would form from the surface, resulting in relatively low brush thicknesses, before the system appeared to self-terminate. This observation was unexpected as the CGC mechanism inherently has no termination reactions and should therefore continue to react to produce high molecular weight polymers and thick brush films. In addition, it was also observed that during the polymerizations using monomers containing the methoxide leaving group, an insoluble by-product was produced during the polymerization. Analysis of this by-product determined it to be lithium methoxide aggregates, produced in solution as part of the polymerization mechanism, which could potentially lower the solubility of the polymer by blocking the ester end groups. When conducting a surface initiated polymerization, these aggregates produced a film on the silica wafer surface, which was hypothesized to block monomer from reaction with the end group of the polymers and, subsequently, inhibit further brush growth.

As a result of these observations, the following study has been conducted to investigate the factors that influence the overall CGC mechanism, kinetics, and by-product stability and solubility. To achieve this, the experiments focused on the nature of the ester leaving group and how this affects the polymerization performance and resulting solubility of the condensation products, along with how they affect the ability to achieve controlled molecular weights and narrow molecular weight distributions.
This study focuses on two different categories of ester monomers: alkyl esters (straight chain and branched), and phenyl derivatives with varying para-substituents (electron donating and electron withdrawing character). To assist in understanding the results obtained in this study, theoretical calculations were also conducted to explain the observed trends with varying ester substituents.

4.2 Experimental Section

4.2.1 Materials

Lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS, 1.0 M) in tetrahydrofuran (THF), dimethylamine solution (2 M, THF), triethylamine (>99.5%), thionyl chloride (SOCl₂, >99.5%), anhydrous dichloromethane (DCM) (stabilized with 50-150 ppm amylene, >99.8%), octanal (99%), sodium triacetoxyborohydride (97%), and MgSO₄ were purchased from Sigma Aldrich. Dichloromethane (DCM), acetic acid, NaHCO₃, NaOH, and ethyl acetate were purchased from Macron. Ammonium chloride (99.9%) was purchased from Baker Scientific and methyl 4-aminobenzoate (98%) from Alfa Aesar. Unless otherwise mentioned, all chemicals were used as received without further purification. THF was purchased from Macron and was purified and dispensed through a PURE SOLV MD-4 solvent purification system (activated alumina, copper catalysts and molecular sieves).

4.2.2 Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on a JEOL-500 S MHz spectrometer. Infrared spectra were recorded on a Thermo Scientific Nicolet iS50 Fourier transform infrared (FTIR) spectrometer using a diamond attenuated total reflectance (ATR) crystal. Number-average molecular weight (Mₙ) and polydispersity index (Mₘ/Mₙ, PDI) were measured using a Viscotek GPCmax gel-permeation chromatography (GPC) unit (eluent: stabilized THF (OmniSolv) with a flow rate of 1.0 mL/min using PLgel 5 μm MIXED-C and MIXED-D columns: molecular weight range 200-2,000,000 and 200-
400.00 g/mol (polystyrene equivalent), respectively. A $dn/dc$ value for the prepared polymers of 0.156 was determined and used during the analysis.

**4.2.3 Synthesis Methods**

**4.2.3.1 Synthesis of Monomers and Initiator**

*Synthesis of N-octyl Monomers*

The following is a representative procedure used for N-alkylation of the various 4-aminobenzoate ester monomers (see Scheme 4.1). The alkylation procedure was adopted from literature\textsuperscript{192} and proved to be very successful for the N-alkylation step of all of the monomers of interest. The synthetic procedures for the corresponding 4-aminobenzoate and initiator precursors is included in Appendix B.

![Scheme 4.1. Alkylation procedure used to synthesize monomers with varying ester groups.](image)

Methyl 4-(octylamino)benzoate (1a)

Methyl 4-aminobenzoate (6.0 g, 38.9 mmol) and octanal (5.0 g, 38.9 mmol) were added to a round bottom flask with dry THF (200 mL). Acetic acid (2.9 mL, 51.3 mmol) and sodium triacetoxyborohydride (9.89 g, 46.7 mmol) were then added, and the flask was
capped with a septum. The solution was stirred overnight at room temperature. The reaction was quenched by adding saturated sodium bicarbonate until the mixture became slightly basic. The product was isolated by extraction with ethyl acetate and washed with brine. After removal of the solvent, the resulting residue was recrystallized from methanol. Product: as white crystals; mp 89-90 °C, (8.3 g, yield 81%).

$^1$H NMR (500 MHz, CDCl$_3$, δ): 7.85 (d, $J$ = 8.9 Hz, 2H, ArH), 6.54 (d, $J$ = 8.9 Hz, 2H, ArH), 4.13 (br, 1H), 3.83 (s, 3H), 3.14 (t, $J$ = 7.4 Hz, 2H), 1.62 (q, $J$ = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3376 (Ar-NH-R), 2946, 2920, 2849 (C-H), 1678 (O-C=O), 1596, 1430, 1190, 1105, 832 cm$^{-1}$

Ethyl 4-(octylamino)benzoate (1b)

Ethyl 4-aminobenzoate (4.5 g, 27.2 mmol), octanal (3.5 g, 27.2 mmol), acetic acid (2.25 mL, 39.2 mmol), and sodium triacetoxyborohydride (6.9 g, 32.7 mmol) used. Product: as white crystals; mp 79-80 °C, (5.1 g, yield 69%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.85 (d, $J$ = 8.9 Hz, 2H, ArH), 6.54 (d, $J$ = 8.9 Hz, 2H, ArH), 4.3 (t, $J$ = 7.4 Hz, 2H), 4.1 (br, 1H), 3.14 (t, $J$ = 7.4 Hz, 2H), 1.62 (q, $J$ = 7.4 Hz, 2H), 1.42-1.22 (m, 13H), 0.88 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3368 (Ar-NH-R), 2921, 2852 (C-H), 1679 (O-C=O), 1596, 1430, 1190, 1105, 835 cm$^{-1}$.

Propyl 4-(octylamino)benzoate (1c)

Propyl 4-aminobenzoate (4.0 g, 22.3 mmol), octanal (2.8 g, 22.3 mmol), acetic acid (1.95 mL, 33.5 mmol), and sodium triacetoxyborohydride (5.68 g, 26.8 mmol) used. Product: as white crystals; mp 66-67 °C, (4.2 g, yield 65%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.85 (d, $J$ = 8.9 Hz, 2H, ArH), 6.54 (d, $J$ = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 4.2 (t, $J$ = 7.4 Hz, 2H), 3.16 (t, $J$ = 7.4 Hz, 2H), 1.75 (m, $J$ = 7.4 Hz, 2H), 1.6 (q, $J$ = 7.4, 2 H) 1.42-1.22 (m, 10H), 1.0 (t, $J$ = 7.4 Hz, 3H), 0.88 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125
MHz, CDCl$_3$, $\delta$): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): $\nu$ = 3372 (Ar-NH-R), 2953, 2923, 2852 (C-H), 1677 (O-C=O), 1600, 1267, 1169, 835, 771 cm$^{-1}$.

**Butyl 4-(octylamino)benzoate (1d)**

Butyl 4-aminobenzoate (4.0 g, 20.7 mmol), octanal (2.6 g, 20.7 mmol), acetic acid (1.8 mL, 31.1 mmol), and sodium triacetoxyborohydride (5.3 g, 25.0 mmol) used. Product: as white crystals; mp 47-48 °C, (4.3 g, yield 62%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.85 (d, $J$ = 8.9 Hz, 2H, ArH), 6.54 (d, $J$ = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 4.2 (t, $J$ = 7.4 Hz, 2H), 3.16 (t, $J$ = 7.4 Hz, 2H), 1.71 (q, $J$ = 7.4 Hz, 2H), 1.62 (q, $J$ = 7.4, 2 H) 1.42-1.22 (m, 12H), 0.95 (t, $J$ = 7.4 Hz, 3H), 0.88 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): $\nu$ = 3381 (Ar-NH-R), 2954, 2928, 2855 (C-H), 1682 (O-C=O), 1600, 1266, 1168, 1104, 831, 769 cm$^{-1}$.

**Isopropyl 4-(octylamino)benzoate (1e)**

Isopropyl 4-aminobenzoate (4.0 g, 22.3 mmol), octanal (2.9 g, 22.3 mmol), acetic acid (1.9 mL, 33.5 mmol), and sodium triacetoxyborohydride (6.1 g, 29.0 mmol) used. Product: as white crystals; mp 90-91 °C, (5.1 g, yield 80%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.85 (d, $J$ = 8.9 Hz, 2H, ArH), 6.54 (d, $J$ = 8.9 Hz, 2H, ArH), 5.2 (m, $J$ = 7.4 Hz, 1H), 4.1 (br, 1H), 3.16 (t, $J$ = 7.4 Hz, 2H), 1.6 (q, $J$ = 7.4, 2 H) 1.42-1.22 (m, 16H), 0.88 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): $\nu$ = 3377 (Ar-NH-R), 2956, 2926, 2854, 1675 (O-C=O), 1600, 1270, 1167, 1100 cm$^{-1}$.

**Tert-butyl 4-(octylamino)benzoate (1f)**

Tert-butyl 4-aminobenzoate (3.0 g, 15.5 mmol), octanal (2.0 g, 15.5 mmol), acetic acid (1.3 mL, 22.4 mmol), and sodium triacetoxyborohydride (3.95 g, 18.6 mmol) used. Product: as white crystals; mp 83-85 °C, (2.6 g, yield 55%). $^1$H NMR
(500 MHz, CDCl$_3$, δ): 7.85 (d, J = 8.9 Hz, 2H, ArH), 6.54 (d, J = 8.9 Hz, 2H, ArH), 4.5 (br, 1H), 3.16 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H) 1.55 (s, 9H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3377 (Ar-NH-R), 2925, 2854, 1678 (O-C=O), 1600, 1153, 1106 cm$^{-1}$.

Phenyl 4-(octylamino)benzoate (1g)

Phenyl 4-aminobenzoate (6.0 g, 28.3 mmol), octanal (3.62 g, 28.3 mmol), acetic acid (2.4 mL, 42.4 mmol), and sodium triacetoxyborohydride (7.8 g, 36.8 mmol) used. Product: as white crystals; mp 112-113°C, (7.3 g, yield 79%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.4 (t, J = 8.1 Hz, 2H, ArH), 7.25 (t, J = 8.1 Hz, 1H, ArH), 7.18 (d, J = 8.1 Hz, 2H, ArH), 6.69 (d, J = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22(m, 10H), 0.88 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3380 (Ar-NH-R), 2921, 2842 (C-H), 1694 (O-C=O), 1594, 1275, 1163, 1075, 742 cm$^{-1}$.

p-Tolyl 4-(octylamino)benzoate (1h)

p-Tolyl 4-aminobenzoate (5.0 g, 22.0 mmol), octanal (2.8 g, 22.0 mmol), acetic acid (1.9 mL, 33.0 mmol), and sodium triacetoxyborohydride (6.1 g, 28.6 mmol) used. Product: as white crystals; mp 105-106°C, (6.1 g, yield 82%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.2 (d, J = 8.2 Hz, 2H, ArH), 7.05 (d, J = 8.2 Hz, 2H, ArH), 6.61 (d, J = 8.9 Hz, 2H, ArH), 4.5 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 1731.4, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3369 (Ar-NH-R), 2919, 2842 (C-H), 1694 (O-C=O), 1595, 1350, 1264, 1056, 835 cm$^{-1}$.

Tert-butylphenyl 4-(octylamino)benzoate (1i)
Tert-butyl 4-aminobenzoate (5.0 g, 18.6 mmol), octanal (2.4 g, 18.6 mmol), acetic acid (1.6 mL, 27.8 mmol), and sodium triacetoxyborohydride (5.1 g, 24.2 mmol) used. Product: as white crystals; mp 130-131 °C, (5.7 g, yield 80%). 1H NMR (500 MHz, CDCl3, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.40 (d, J = 8.9 Hz, 2H, ArH), 7.1 (d, J = 8.9 Hz, 2H, ArH), 6.58 (d, J = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 19H), 0.88 (t, J = 7.4 Hz, 3H). 13C NMR (125 MHz, CDCl3, δ): 165.6, 152.7, 149.0, 148.2, 132.3, 126.3, 121.2, 117.2, 111.4, 99.9, 43.5, 134.5, 31.8, 31.5, 29.45, 29.40, 29.33, 27.2, 22.75, 14.2.; FTIR (ATR): ν = 3371 (Ar-NH-R), 2956, 2929, 2853 (C-H), 1692 (O-C=O), 1599, 1356, 1265, 1163, 1061, 835, 808 cm⁻¹.

p-Methoxyphenyl 4-(octylamino)benzoate (1j)

p-Methoxyphenyl 4-aminobenzoate (6.0 g, 24.7 mmol), octanal (3.2 g, 24.7 mmol), acetic acid (2.2 mL, 37.0 mmol), and sodium triacetoxyborohydride (6.8 g, 32.1 mmol) used. Product: as white crystals; mp 130-131 °C, (7.2 g, yield 82%). 1H NMR (500 MHz, CDCl3, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.1 (d, J = 8.9 Hz, 2H, ArH), 6.9 (d, J = 8.9 Hz, 2H, ArH), 6.58 (d, J = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 3.8 (s, 3H), 3.18 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). 13C NMR (125 MHz, CDCl3, δ): 165.8, 157.1, 152.6, 144.9, 132.3, 122.7, 119.2, 114.5, 111.4, 55.7, 43.5, 31.8, 29.45, 29.40, 29.33, 27.2, 22.75, 14.2.; FTIR (ATR): ν = 3378 (Ar-NH-R), 2956, 2929, 2853 (C-H), 1692 (O-C=O), 1597, 1349, 1282, 1165, 1074, 836, 765 cm⁻¹.

Trifluoromethylphenyl 4-(octylamino)benzoate (1k)

Trifluoromethylphenyl 4-aminobenzoate (5.0 g, 17.8 mmol), octanal (2.3 g, 17.8 mmol), acetic acid (1.5 mL, 26.7 mmol), and sodium triacetoxyborohydride (4.9 g, 23.1 mmol) used. Product: as white crystals; mp 129-130 °C, (4.9 g, yield 70%). 1H NMR (500 MHz, CDCl3, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.7 (d, J = 8.9 Hz, 2H, ArH), 7.3 (d, J = 8.9 Hz, 2H, ArH), 6.59 (d, J = 8.9 Hz, 2H, ArH), 4.25 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). 13C NMR (125 MHz, CDCl3,
δ): 164.9, 152.9, 132.5, 126.7 (q, J = 3.8 Hz) (C-F), 122.5, 116.2, 111.5, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0. 19F NMR 1 peak; FTIR (ATR): ν = 3376 (Ar-NH-R), 2952, 2924, 2854 (C-H), 1698 (-CO-O), 1598, 1320, 1272, 1159, 1120, 1058, 833, 761 cm⁻¹.

**Synthesis of Initiator**

The synthesis scheme for the phenyl initiator can be seen in Scheme 4.2.

Scheme 4.2. Synthesis of dimethyl amide phenyl ester initiator (DMA-P).

**Phenyl 4-(dimethylcarbamoyl)benzoate (DMA-P Initiator)**

In a 100 mL round bottom flask, with a stir bar, was placed 4-(phenoxy carbonyl)benzoic acid (1.1g, 4.5 mmol) and SOCl₂ (11 mL, 150 mmol). The mixture was refluxed until the acid dissolved, producing the acid chloride. Excess SOCl₂ was removed under vacuum. The remaining acid chloride was dissolved in anhydrous DCM (30 mL). A solution of dimethylamine (2M in THF) (2.73mL, 5.5 mmol), triethylamine (0.7mL, 5.0 mmol), and DCM (20 mL) was prepared and added slowly to the acid chloride. The mixture was refluxed for 1 h. The solvent was then removed under vacuum, the residue was dissolved in ethyl acetate and passed through a short column (eluted with ethyl acetate). After removal of the solvent and drying under vacuum, no further purification was necessary. Product: as white crystals; mp 111-112 °C, (0.86g, yield 70%). 1H NMR (500 MHz, CDDI₃, δ): 8.2 (d, J = 8.1 Hz, 2H, ArH), 7.54 (d, J = 8.2 Hz, 2H, ArH), 7.42 (t, J = 8.0 Hz, 2H, ArH), 7.27 (t, J = 8.0 Hz, 1H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH), 3.1, (s, 3H) 2.97 (s, 3H) (N-CH₃); 13C NMR (150 MHz, CDCl₃, δ): 170.5, 164.6,
150.9, 141.4, 130.46, 130.40, 129.6, 127.3, 126.1, 121.7, 39.4, 35.4; FTIR (ATR): ν =
3085, 2920, 1724 (O-C=O), 1616 (N-C=O), 1393, 1265, 1085, 876, 720 cm\(^{-1}\).

4.2.3.2 Polymerization Methods

*Solubility Experiments*

A representative procedure is outlined below for the methyl ester monomer (1a) at room
temperature, where the only difference between other monomer experiments is the nature of the monomer, with the molar amounts remaining the same. A typical polymerization procedure utilizing the DMA-P initiator and the monomer of interest is depicted below in Scheme 4.3. The monomer 1a (0.264 g, 1.0 mmol) and DMA-P initiator (6.8 mg, 0.025 mmol) were placed in a flask, purged with argon for 5 min, followed by the addition of THF (20 mL) via syringe and needle. The LiHMDS base (1.1 mL, 1.1 mmol) was then injected and the solution was stirred for 12 h at 20\(^°\)C. Qualitative solubility observations were then collected, observing the opacity of the resulting solution. The polymer was then isolated via extraction with dichloromethane, and purified by washing with a NaOH/brine solution, dried over MgSO\(_4\) and isolated by removing the solvent and by products under vacuum before further drying in a vacuum oven at 60\(^°\)C for 2 h.

*Kinetics Experiments*

A representative procedure is outlined below for the methyl ester monomer (1a) at room temperature, where the only difference between other monomer experiments is the nature of the monomer, with the molar amounts remaining the same. The monomer 1a (0.132 g, 0.5 mmol) and DMA-P initiator (3.4 mg, 0.025 mmol) were placed in a flask, purged with argon for 5 min, followed by addition of THF (10 mL) via syringe and needle. The resulting solution was then brought to the desired temperature (20\(^°\)C). For other polymerizations, a room temperature bath was achieved with a monitored (20\(^°\)C) water bath, an ice bath was used for 0\(^°\)C, a saturated brine bath was used for -20\(^°\)C, dry ice and acetonitrile was used for -48\(^°\)C, and dry ice/acetone was
used for the -78°C reaction temperature. The LiHMDS base (0.6 mL, 0.6 mmol) was then injected, thus starting the reaction. The polymerization was then allowed to proceed for the desired amount of time followed by removal of a 1 mL aliquot for analysis, which was quenched by addition to an aqueous saturated ammonium chloride solution. The polymer workup remained the same as listed above to isolate the converted polymer. NMR and GPC experiments were used to determine subsequent conversion, molecular weights, and molecular weight distributions.

![Scheme 4.3. Polymerization scheme using DMA-P initiator and octyl monomers with varying ester R substituents.](image)

4.2.3.3 Computation Modeling Parameters

All computations used the high-performance computing facility accessible through Colorado School of Mines. The Gaussian 09 package was utilized for density functional theory (DFT) calculations performed during this study. Geometry optimizations were performed using the 2006 version of the Global hybrid Minnesota functional (M06-2X) and the split valence polarized
basis set 6-31+G(d).\textsuperscript{203,204} Implicit solvation of THF was incorporated into the calculations using the integral equation formalism variant polarizable continuum mode (IEFPCM).\textsuperscript{205} The minimum energy structures were characterized by the absence of any imaginary frequencies while the transition states were confirmed the presence of an imaginary frequency. Nature of the transition state was confirmed by following IRC calculations. Partial atomic charges were computed using a Natural Bond Orbital (NBO) analysis.\textsuperscript{206} Activation energies and reaction rates for the polymer growth mechanism were obtained using the aforesaid calculations in the KisTheIP package.\textsuperscript{207}

### 4.3 Results and Discussion

The vast majority of literature on application of the CGC technique involves the polymerization of methyl ester monomers, which have proved to be mostly successful in producing defined polymers and also produces low-boiling point byproducts.\textsuperscript{116,124,192} Based on this literature, we hypothesized that the methyl monomer would be a good candidate for the preparation of aramid brushes via CGC polymerization in our original work.\textsuperscript{6} However, in this work it was observed that control over the polymerization was only achieved up to a degree of polymerization (DP) of approximately 80, which also corresponds to literature studying solution polymerizations of the same monomer.\textsuperscript{192} The proposed mechanism for CGC suggests that control over the polymerization is primarily achieved when the end group of the polymer is selectively available for reaction with the amide anion nucleophile. In our previous polymer brush paper it was observed that during the polymerization of the methyl ester monomer, the solution turned from a clear yellow solution to a very cloudy, almost slurry, towards the completion of the reaction. As formation of the insoluble product corresponded to loss of control in the polymerization, we hypothesized that control is lost as a result of either the diminished solubility of the produced polymer or insoluble condensation by-products. Both the diminished solubility of the polymer or the presence of an insoluble film on the surface of the polymer brush would
decrease the end groups availability for attack by the amide nucleophile, thus losing control over the polymerization.

In an effort to obtain better control over the polymer molecular weight and also produce polymers of low polydispersity it is important to understand the CGC polymerization mechanism. A depiction of the polymerization propagation reaction is shown in Scheme 4.4. Before the monomer can add to the active polymer end group, it must be deprotonated by the strong non-nucleophilic base LiHMDS. The reactive monomer can then add to either the initiator or the end group of a growing polymer’s ester group to give a tetrahedral intermediate transition state. This intermediate can then either return to the original reactants or rearrange to eliminate the ester alkoxide, leaving the polymer chain with one additional monomer and the lithium alkoxide as the by-product. Scheme 4.4 highlights the importance of the electrophilicity of the carbon of the ester carbonyl, the basicity of the ester alkoxide, and the solubility of the lithium alkoxide in propagation of the polymer chain and, hence, control over the CGC polymerization.

Scheme 4.4. Polymerization mechanism for nucleophilic acyl substitution at the ester carbonyl group during addition of monomer to the propagating polymer chain.

Common to each of these factors is the structure of the monomer ester group, thus designing polymers using monomers with different ester groups should allow for a better
understanding of the factors that affect the formation of well-defined polymers using the CGC technique by examining the solubility of the produced by-products and reactivity of the ester polymer end group.

4.3.1 Solubility of Lithium Alkoxides and Phenoxides

In an effort to address the solubility issue attributed with CGC polymerization of the methyl ester monomer, the solubility of different lithium alkoxides and phenoxides was investigated. Changing the ester substituent on the monomer will allow for the production of different lithium alkoxides after the nucleophilic acyl substitution reaction at the polymer end group. The ester substituent also has the potential to change the reactivity and solubility of both the polymer end group and the resulting lithium alkoxides. The preliminary study used this to investigate the solubility of the alkoxide produced from the different ester monomers was to recreate the conditions of post-polymerization by deprotonating the candidate parent alcohols, using LiHMDS, and create the lithium alkoxide in a THF solution. For example, the solution of lithium methoxide was prepared by addition of LiHMDS to a THF solution of methanol at the same concentration as they would be in the polymerization solution. The results showed that the lithium methoxide salt was indeed insoluble, due to the fact that it produced a cloudy suspension under these conditions. However, it was observed that all other aliphatic alcohols of interest: ethyl, propyl, butyl, isopropyl, and tert-butyl, yielded much clearer solutions under the same conditions, suggesting they produced a more soluble lithium alkoxide in THF. In addition, we also investigated various lithium phenoxides as other potential ester monomer candidates. Phenol, along with para-substituted phenols (p-cresol, 4-tert butyl phenol, p-methoxy phenol and 4-trifluoromethyl phenol), were mixed with 1 equivalent of LiHMDS in THF. The results demonstrated that all systems produced clear solutions, suggesting that lithium phenoxide salts also have good solubility in THF. There are few examples examining the solubility of lithium alkoxides and phenoxides in literature. Kamienski and Lewis have
conducted the most detailed study of the solubility of lithium alkoxides, concluding that alkoxides with branching have increased solubility in hydrocarbon solvents and ethers but lower solubility in alcohols. While this work also demonstrated that the solubility of straight chain alkoxides in ethers and hydrocarbons is low, they did observe a slight increase in solubility as the chain length of the alkoxide increases.

Understanding the reasons for the variation in the solubility of the different lithium alkoxides and phenoxides is a difficult and complex task. While Kamienski attributed the differences in solubility in hydrocarbon and ether solvents to different degrees of polymerization or aggregation of the alkoxides, Arnett demonstrated that there was no obvious relationship between the aggregation number of lithium alkoxides and the basicity of the corresponding anion and, in conjunction with the observation that there was an equilibria between different aggregation states, concluded that there are only small differences between the relative stabilities of different aggregation states. Despite the complexity of this area, it was decided in order to proceed with the current investigation, only monomers that produced soluble conjugate lithium alkoxides or phenoxides, based upon the previous solubility tests, would be prepared and used to investigate the effect of different leaving groups on the CGC polymerization performance.

4.3.2 Polymerization of Alkyl Ester Derivatives

Solubility

The polymerization of the n-alkyl ester monomers 1b-1d all yielded solutions that appeared optically very similar to the methyl ester monomer 1a, producing opaque solutions despite the hypothesis that increasing the length of the alkyl chain would produce more soluble lithium alkoxides and the results of the lithium alkoxide solubility tests described above. However, it was noticed that the longer the alkyl chain of the ester, the less cloudy the final polymerization solution, although all of the solutions had some degree of opacity. In comparison, the resulting
polymerization solutions for the branched isopropyl and tert-butyl ester monomers 1e and 1f, respectively, produced clear solutions. The branched ester results demonstrate that while the branched alkoxides follow the observations of the previous alkoxide solubility tests, the n-alkyl alkoxides do not, in that they produced insoluble products. However, they do agree with observations in literature.

The reason for the varying solubility results for the alkyl esters is most likely due to the fact that the aggregation states for lithium alkoxides are strongly dependent on temperature, concentration, and solvent type. While the longer alkyl chain alkoxides theoretically make the aggregates more soluble, each of these systems produced some degree of insoluble materials during the polymerization, despite the good solubility demonstrated by all aliphatic alkoxides, except lithium methoxide, in the solubility studies at concentrations equivalent to the polymerization system. These results suggest that the presence of monomer and/or polymer in solution changes the solubility of the alkoxides, resulting in some degree of insolubility for all of the n-alkyl alkoxides, however good solubility for the branched alkoxides was maintained.

Kinetics

To investigate the properties of the alkyl ester monomers further, kinetic studies were performed. These studies demonstrated that even though the straight chain ester monomers polymerize under the conditions utilized, they would all reach a limiting conversion, where the extent of conversion decreased with increasing alkyl chain length. In a comparison between the methyl and ethyl ester monomers, seen in Table 4.1, it is evident that under the same reaction conditions of 12 hours at 20°C, the ethyl monomer only reaches 95% conversion, with slightly higher PDI. These results are similar to previous results in literature for a meta monomer system investigating the utilization of ethyl esters. The kinetics performed on the ethyl ester also shows that the ethyl ester proceeds at a slightly slower rate, due to its lower experimental rate constant of propagation, \( k_p \), being less than half of the methyl monomer’s.
Table 4.1. Comparison between the polymerization results of methyl and ethyl ester substituents.

<table>
<thead>
<tr>
<th>Ester</th>
<th>Conversion (%)</th>
<th>MW (NMR)</th>
<th>PDI (GPC)</th>
<th>$k_p$ (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>100</td>
<td>8240</td>
<td>1.09</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethyl</td>
<td>95</td>
<td>8040</td>
<td>1.11</td>
<td>0.11</td>
</tr>
</tbody>
</table>

In comparison to the n-alkyl ester monomers, the polymerization of the monomers that contain the isopropyl and tert-butyl esters (1e and 1f) yielded some interesting results. Based on kinetic studies, it was observed that the isopropyl monomer (1e) polymerizes at a significantly slower rate than the n-alkyl esters, despite maintaining solubility throughout the polymerization. It was noticed, however, that after reaching a critical conversion of 38% the reaction would appear to terminate. It was also observed that the tert-butyl ester monomer (1f) had no reactivity towards polymerization, with no conversion achieved even after a long reaction period of 2 days or by conducting the reaction under reflux conditions.

The variation in kinetic results of the alkyl ester monomers can be explained by both the sterics and the relative basicity of alkoxide produced as a result of the nucleophilic acyl substitution propagation reaction. In terms of sterics, it is hypothesized that increased branching on the ester alkoxide increases the activation energy for formation of the tetrahedral intermediate due to crowding around the electrophilic carbon of the carbonyl as the nucleophile approaches. In addition, the rate of aminolysis of the ester end group of the polymer chain is dependent on the relative basicity of the alkoxide leaving group, with breakdown of the tetrahedral intermediate to the amide product and alkoxide by-product favoured by a less basic alkoxide or more acidic conjugate acid of the alkoxide leaving group (Table 4.2). The pKa of the conjugate acid of tert-butoxide, tert-butanol, has the highest pKa of 19.2 with a gradual decrease in pKa with a decrease in both branching and n-alkyl chain length to the simplest alkoxide, methanol at a pKa of 15.5.\textsuperscript{211} Both of these factors contribute to the decreased reactivity of the two branched ester derivatives,
with the increased steric hindrance and high pKa of the tert-butyl group producing an essentially inert system under the conditions used.

Table 4.2. pKa values of conjugate acids corresponding to the lithium alkoxides produced as by-products. *Values from Perrin.²¹¹

<table>
<thead>
<tr>
<th>Conjugate Acid</th>
<th>pKa a @25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-butanol</td>
<td>19.2</td>
</tr>
<tr>
<td>isopropanol</td>
<td>17.1</td>
</tr>
<tr>
<td>n-butanol</td>
<td>16.1</td>
</tr>
<tr>
<td>n-propanol</td>
<td>16.1</td>
</tr>
<tr>
<td>ethanol</td>
<td>16.0</td>
</tr>
<tr>
<td>methanol</td>
<td>15.5</td>
</tr>
<tr>
<td>H₃CO-phenol</td>
<td>10.8</td>
</tr>
<tr>
<td>(H₃C)₃C-phenol</td>
<td>10.4</td>
</tr>
<tr>
<td>H₃C-phenol</td>
<td>10.1</td>
</tr>
<tr>
<td>phenol</td>
<td>9.9</td>
</tr>
<tr>
<td>F₃C-phenol</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Based on the above results, it was concluded that the alkyl ester monomers produce polymer solutions containing insoluble by-products and/or have low polymerization rates, both of which limit the ability to obtain a well-controlled polymerization and produce well-defined polymers. As a result, our attention was subsequently focused on utilizing the phenyl ester monomers.

4.3.3 Polymerization of Phenyl Esters Derivatives

Solubility

The phenyl ester monomer has been previously utilized to prepare a variety of aramid structures by CGC polymerization and is typically the ester of choice with these polymerizations, due to its relatively high reactivity.¹¹⁸-¹²² In addition, the preliminary solubility studies discussed above demonstrated that the resulting solutions for all of the tested phenoxides, derived from the phenyl ester monomers (1g-1k), produced very soluble by-products. Based on these factors, the effectiveness of the different phenyl ester monomers was investigated. Initial polymerizations demonstrated that these monomers (1g-1k) all produced clear solutions throughout the course of
the reaction, demonstrating that the polymer formed stayed in solution and the condensation by-products formed are also soluble under these conditions. Unlike the lithium alkoxides, there is very little data in the literature regarding the solubility of lithium phenoxides. Arnett demonstrated the solubility of a wide range of phenol derivatives in THF, after deprotonation with LiHMDS, while studying the aggregation numbers of a variety of lithium salts. In this study, all of the lithium phenoxides examined, except that produced after deprotonation of methyl 4-hydroxybenzoate, were soluble in THF at a concentration of 0.10 M. The excellent solubility of all components of the polymerization process when using phenyl ester monomers allowed for a kinetic study to determine the control over the polymerization reaction without having to be concerned with competing precipitation reactions.

Kinetics

A series of experiments were performed on the phenyl ester monomers that focused on kinetics studies to examine the effect of substitution on the reactivity of the different monomers (1g – 1k). Each kinetics experiment consisted of taking four samples at a given temperature and conversions were monitored using NMR. As can be seen in Figure 4.1, the molecular weight obtained using NMR, by taking the ratio of the polymer proton signals to the initiator proton signals, show good agreement with the theoretical molecular weight and gives a linear relationship when plotted against the conversion of monomer, indicating a constant concentration of chains in the polymerization system.
Figure 4.1. Relationship of number average molecular weight ($M_n$) and molecular weight distribution with conversion for the four monomers of interest.

The kinetic semi-logarithmic plots of conversion versus time were obtained by examining the conversion, using NMR, throughout the polymerization (Figure 4.2). Specifically, the monomer conversion was computed using the ratios of monomer and polymer NMR proton signals adjacent to the nitrogen amide (polymer) or amino (monomer) group on the benzene ring. Figure 4.2 demonstrates that a linear relationship was obtained for each system at a reaction temperature of $-20^\circ$C, indicating a constant number of active species in the polymerization. The reaction temperature of $-20^\circ$C was chosen as it was found to be the lower end of the temperature range for maintaining a controlled polymerization for the slower monomers, while also being the upper temperature range for the fastest trifluoromethylphenyl ester monomer (1k). The linear first order kinetic relationship in the semi-logarithmic plots allows for determination of the experimental
propagation rate constant, $k_p$, from the slopes of the plots. The calculated $k_p$ values (Figure 4.2) demonstrate that the trifluoromethylphenyl ester monomer is the most reactive with a $k_p = 14.3 \text{ s}^{-1}$, which is the orders of magnitude faster than the slowest monomer, the methyl ester, with a $k_p = 0.013 \text{ s}^{-1}$. The molecular weight distribution with time was also monitored via GPC. Figure 4.3 shows the molecular weight distributions for the fastest p-trifluoromethylphenyl ester monomer (1k) as a function of time at -20°C. These traces show that the polymer peak is monomodal throughout the course of the reaction and maintains a narrow molecular weight distribution with the PDI values ranging from 1.09 to 1.11. The other peak at a retention volume near 18 mL, is due to monomer and shows a decreases with time as the monomer in the system is consumed and the reaction reaches completion in under 5 minutes.

![Figure 4.2. Polymer kinetics studied for various ester monomers at -20°C. The experimental propagation rate constants were calculated from the slope of the plots and the initiator concentration.](image)
Figure 4.3. GPC traces demonstrating molecular weight and molecular weight distribution evolution for the trifluoromethylphenyl ester monomer (1k) at -20°C.

The main focus of the kinetic studies was to study how the para substituents on the phenyl ester monomer affects the overall polymerization process. Conventional understanding in the literature is that well defined chain growth polycondensation polymers are prepared by converting the traditional step growth process into a chain growth process by deactivating the ester substituent on the monomer. This is achieved by deprotonation of the amine on the monomer by strong base, with the resulting amide anion donating electron density to the ring and effectively making the carbonyl carbon of the ester less electrophilic and, hence, less reactive to nucleophilic acyl substitution. Decreasing the reactivity of the carbonyl carbon is assumed to limit the monomer-monomer reactions typically observed in step growth polymerizations. Based on the results in this study, the reactivity of the monomer towards nucleophilic acyl substitution is a
function of more than just the carbonyl electrophilicity; it is also strongly influenced by the basicity of the leaving alkoxide. As discussed previously, Scheme 4.4 depicts the nucleophilic acyl substitution mechanism for addition of monomer to the polymer end group.

From this mechanism it is apparent that formation of the tetrahedral transition state has an energy barrier that is associated with the reactivity and, hence, the kinetics, of the polymerization system. The process where the alkoxide is forced away from the tetrahedral intermediate plays a great role on how efficiently the process happens. What we believe we are observing is that the more stable the negative charge, is more easily ejected from the intermediate complex, making the process more “reactive.” The stability mentioned herein refers to how well the negative charge is delocalized and “stabilized,” and can be related to the pKa of the alkoxides conjugate acid, or the parent alcohol. A Table of the conjugate acid of the alkoxides of interest can be seen in Table 4.2.

It is apparent in the table that the pKa is highest for the most bulky alkyl alcohol, tert-butanol with a value of 19.2, followed by isopropanol, n-linear alkanes, ethanol and finally methanol at 15.5. This can be explained by the more electron “donating” character of the alkyl groups destabilizing the charge, making the deprotonating process less favourable. There is a large jump in pKa from methanol ~15 to phenol ~10 derivatives due to the ability of the phenyl unit to stabilize the resulting negative charge through resonance. There is an obvious trend observed when examining the para substituents on the phenyl ring. When the ring has electron donating groups such as methoxy and weakly donating alkyl groups the pKa drops from 10.8 to the unsubstituted phenol at a pKa of 9.9. The pKa continues to drop with the increasing acidity and stability of the electron withdrawing character of trifluoromethyl group with a pKa of 8.7.

4.3.4 Determination of Activation Energies

Kinetic data was collected for all of the phenyl ester derivative monomers, along with the methyl monomer (1a), since it was the only alkyl ester monomer where full conversion was
achieved. From this data, the experimental propagation constants were calculated for each monomer at three temperatures. For all of the monomers, excluding the trifluoromethyl phenyl monomer, polymerizations were run at 20, 0, and -20°C. These temperatures were chosen because the kinetics for these monomers at these particular reaction conditions was slow enough where samples could be taken within a reasonable amount of time. The three temperatures chosen for the trifluoromethyl phenyl monomer (1k) were -20, -48 and -78°C, due to the very high reactivity of this monomer. It was found that above these temperatures, the reaction was complete in less than a minute and the polymers produced had high PDIs, near 1.7-1.8, demonstrating a lack of control in the polymerization process. The kinetic data was then used to determine the activation energy of the various reactions via a plot of the log the experimental propagation constant, $k_p$, versus $1/T$ to yield a linear relationship (Figure 4.4). A complete list of activation energies are summarized in Table 4.3.

![Figure 4.4. Arrhenius relationships for the various ester monomers. The activation energies ($E_a$) were calculated from the slopes of the plots.](image)
Table 4.3. Extracted Arrhenius data including the slope, intercept, and calculated activation energies for the monomers examined.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Slope (K)</th>
<th>Intercept</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₃C-Ph</td>
<td>4197.6</td>
<td>19.3</td>
<td>34.9</td>
</tr>
<tr>
<td>Phenyl</td>
<td>4359.5</td>
<td>16.8</td>
<td>36.2</td>
</tr>
<tr>
<td>H₃C-Ph</td>
<td>4424.6</td>
<td>17.6</td>
<td>36.8</td>
</tr>
<tr>
<td>(H₃C)C-Ph</td>
<td>4847.8</td>
<td>18.9</td>
<td>40.3</td>
</tr>
<tr>
<td>H₃CO-Ph</td>
<td>5364.1</td>
<td>20.5</td>
<td>44.6</td>
</tr>
<tr>
<td>Methyl</td>
<td>6188.3</td>
<td>51.5</td>
<td>51.5</td>
</tr>
</tbody>
</table>

The activation energies obtained from the kinetic experiments closely follows the reactivity trend for the different monomers presented above. The slowest monomer studied in the kinetics study, the methyl ester monomer (1a), also has the highest slope and hence, the highest activation energy. Whereas, the much faster phenyl ester monomers have significantly lower activation energies when compared to the methyl system. Within the phenyl ester monomers, there was also an observable trend with the activation energy increasing with increasing electron donating character of the para substituent. The electron withdrawing trifluoromethyl substituent has the lowest activation energy and is observed to be the fastest monomer, while also demonstrating a controlled polymerization at very cold temperatures, -48 and -78°C. The much slower phenyl and p-methoxy phenyl monomers (which show no conversion at the coldest temperature, -78°C for up to 6 hours) also follow this trend, where the reactivity is reduced with more electron donating character of the methoxy substituent compared to the unsubstituted phenyl ester monomer.

The general reactivity trend of esters reported above agrees, to a certain degree, with literature on the reactivity of small molecule esters with various nucleophiles. The hydrolysis of esters has been studied extensively and it has been observed that the p-substituent of the ester plays a key role in determining its reactivity. Mitton and co-workers reported that, for hydrolysis of
various esters, the fate of the leaving groups also depends on the relative basicity after leaving the tetrahedral intermediate adduct. In more relevant studies, Menger and co-workers examined the aminolysis of esters in protic solvents and demonstrated that the rate determining step of the reaction is related to the stability of the alkoxy leaving group. In addition, recent theoretical work investigating the aminolysis mechanism of methylamine with methyl acetate proposed that there may be an existence of a mechanism that bypasses the tetrahedral intermediate. The two separate mechanisms put forward were the direct substitution reaction, where the exchange occurs in a concerted pathway and an exchange that is assisted by a 2(1H)-pyridone catalyst. The conclusion of this work suggest that there are alternative mechanisms that could explain the behaviour of aminolysis reactions and the mechanisms have the potential to be quite complex. However, these studies were conducted with the protonated amine exchanging with the more stable leaving alcohol and there is very little discussion in the literature of the mechanisms of lithiated basic aminolysis under aprotic conditions. Despite the agreement between the results obtained here and the literature on nucleophilic acyl substitution using small molecules, this study represents the first detailed investigation on the effect of the ester leaving group on CGC polymerization.

4.3.5 Computational Modelling - Activation Energies and Charges

To gain a better understanding of the experimental results presented above, DFT calculations were performed on the CGC polymerization mechanism. The octyl group in the monomers was replaced with methyl group to reduce the computational cost (Scheme 4.5). A natural bond orbital (NBO) analysis was performed to gain insight on the electrophilic nature of the ester carbonyl groups involved in the formation of the tetrahedral intermediate and the cleavage of the alkoxy product. Additionally, transition state calculations were performed to determine the role of electrophilicity of carbonyl carbon, stability of the leaving group and formation of tetrahedral
intermediate plays in the reaction energetics. Transition state calculations were also used to obtain the activation barriers for the overall mechanism.

Scheme 4.5. Model system employed for computational studies. The charges of the three esters of interest were calculated for the phenyl ester monomer system, along with the charges for varied esters.

Electrophilicity of Ester Carbonyls

As discussed previously, it is well understood that control over CGC polymerizations for the production of aramids is established when the reactivity of the monomer is higher with the ester on the initiator or polymer end group than the ester on another monomer, resulting in reactions following a chain growth process. Literature proposes that “deactivation” of the monomer is achieved by the deprotonation of the aromatic amine on the monomer, thus producing an amide ion that donates charge to the ring and, is thought to, “shield” the carbonyl from attack by another deprotonated monomer.\textsuperscript{112} To examine this proposed mechanism for obtaining a chain growth process, an NBO analysis was performed to calculate the partial atomic charge on the carbon of the carbonyl group for the various species in the reaction. The effective electrophilicity of the carbonyl carbon was gauged by calculating relative atom charges for atoms including, and surrounding, the carbonyl groups involved in a CGC reaction (Species 1 2 and 3 from Scheme
4.5). Similar calculations on various leaving groups were also performed to assist the understanding of the trends observed when changing the substituent to more reactive esters presented later. To the best of our knowledge, this is the first computational study of the CGC polymerization system for the preparation of aramids.

The first computation study performed was to support the claim that the electrophilicity of the ester carbonyl carbon is reduced for the deprotonated monomer when compared to the polymer end group. NBO calculations were performed on the particular system presented in Scheme 4.5 containing the phenyl R group to predict the inherent electrophilicity by computing the charge on the carbonyl carbon, along with the surrounding oxygen atoms for reference. This experiment was used to compare the relative charges of species present in a typical reaction mixture to investigate which species would be the most reactive between the polymer end group (5.1Ph), the deprotonated monomer (5.2Ph), and a polymer end group with one additional monomer (5.3Ph).

The computed charges seen in Table 4.4 show that the charge on the carbonyl carbon of compound 5.1Ph is similar to 5.3Ph. This suggests that the electrophilicity or "charge" of the carbonyl carbon on the polymer end group remains the same after monomer addition. Also, calculations show that the deprotonated monomer, 5.2Ph, has a smaller positive charge on the carbon of the ester carbonyl when compared to the polymer end group, due to the donated negative charge from the deprotonated nitrogen. This demonstrates that the reactive monomer does indeed have a less electrophilic carbonyl carbon, suggesting that the reactivity of the ester on the monomer is reduced when compared to the polymer end group. These results explain why addition of the deactivated monomer preferentially occurs at the growing polymer end group or at an initiator, if any of those species are present and also agrees with the argument put forth by the Yokozawa group, when explaining how to convert step-growth polymerizations to a chain growth process.\textsuperscript{112}
Table 4.4. Charges computed for atoms surrounding the carbonyl participating in the nucleophilic attack for the three carbonyl species depicted in Scheme 5 with a phenyl R group.

<table>
<thead>
<tr>
<th>Atom (in bold)</th>
<th>Carbonyl Investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>-0.557</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>0.854</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>-0.584</td>
</tr>
</tbody>
</table>

Even though literature focuses on the idea that the polymer end group and monomer reactivity is primarily affected by the relative electrophilicity, or activation/deactivation, of the carbonyl carbon of the ester group, the results previously discussed in this study demonstrate that the reactivity is also greatly affected by the ester substituent. To examine these observations, computational studies were also conducted to examine the effect of the ester substituent on the relative electrophilicity of the various ester carbonyl carbons (Table 4.5). As such, the charges on the carbon and oxygen atoms of the ester carbonyl were calculated for a phenyl ester monomer with various substituents in the para position. The charges in Table 4.5 were calculated for species 2 and 3 (Scheme 4.5) using different R group ester substituents. These calculations show that variation of the phenyl ester substituent shows very little effect on the electrophilic nature of the carbonyl carbon and, in fact, the only trend observed is opposite to what would be expected regarding electrophilicity and reactivity of the different monomers. Table 4.5 shows that electron withdrawing groups, such as the trifluoromethyl group, tend to be the only groups that significantly change the charge on the carbonyl carbon atom, however, they make the carbon less electrophilic. This observation is actually in agreement with a similar analysis performed by Neuvonen and coworkers investigating the electrophilicity of small molecule esters with varying electron withdrawing character in the ester substituent. This effect can be explained by variation in the amount of charge on the carbonyl oxygen in the ester substituent. The electron withdrawing group on the ester substituent results in less negative charge on the carbonyl oxygen, which produces less polarization on the carbon that shares the bond with oxygen. This decrease in
polarization produces less positive charge on the carbonyl carbon, suggesting that it is less electrophilic. The opposite is observed for the electron donating groups, making the carbonyl carbon more electrophilic. These results, while expandable, contradict the experimental observations, with the trifluoromethyl phenyl ester monomer showing the fastest rate of reaction in the kinetic experiments despite the computational results showing it’s ester carbonyl carbon has the lowest positive charge.

Table 4.5. Charges calculated for atoms surrounding the carbonyls present during a CGC reaction conditions with phenyl R group and methyl leaving group for comparison. *A basis set without diffuse functions was used to calculate NBO charge as an error in Gaussian code prevents calculation.

<table>
<thead>
<tr>
<th>Atomic Charge (in bold)</th>
<th>5.2</th>
<th>5.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ph</td>
<td>Ph-CH₃</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>-0.581</td>
<td>-0.581</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>0.814</td>
<td>0.814</td>
</tr>
<tr>
<td>O=C-OR</td>
<td>-0.687</td>
<td>-0.686</td>
</tr>
</tbody>
</table>

While the electrophilicity of the carbon of the acyl group plays a significant role in the reactivity of the monomer in the polymer mechanism, our results demonstrate the stability of the leaving group may actually be the main driving force for the experimental trends observed. The experimental results show that there is a major difference between the kinetics of the methyl ester monomer (1a) when compared to the phenyl ester monomer (1g). This is because the methoxy leaving is very unstable whereas the phenoxy leaving can stabilize via resonance stabilization. Incorporating an electron donating group in the para position reduces the stabilization of the leaving group whereas an electron withdrawing group facilitates the resonance stabilization leading to a more stable phenyl alkoxide resulting in a faster overall polymer growth mechanism.

These trends are observed in the computed thermodynamics and kinetics of the mechanism and are in agreement with experimental results; see Table 4.6.
The calculated energies are in good agreement with the experimental activation energies in trends alone, and both reveal that the activation energies for the polymer growth mechanism are largely affected by the leaving group substituent group. The tert-butyl ester has the largest barrier to overcome in order for the reaction to proceed with no experimental activation energy obtained, followed by a lower activation energy of the more successful methyl ester. We believe that steric s and high pKa’s contributes to the large activation energy observed for the tert-butyl group, and only the basicity of the less hindered methoxide anion contributes to the low but successful reactivity of the ester. The lower energy barriers attributed to the phenyl esters correspond to the lower basicity and higher anion stabilization, especially with the electron withdrawing trifluoromethyl group and facilitate the phenoxide ejection portion of the mechanism. The electron withdrawing group helps to pull charge into the ring, stabilizing the negative charge of the leaving group. However, donating groups push the charge onto the oxygen making it harder to separate after attack from the amide nucleophile.

**4.4 Conclusions**

One attempt to improve upon the well-studied literature surrounding the polymerization of the “convenient” methyl ester aminobenzoate monomers, studies were performed to investigate the potential use of monomers with varying ester substituents. Monomers with
varying ester groups ranging from n-alkyl and branched esters to substituted phenyl esters were synthesised and polymerized to study the solubility and polymerization effectiveness. Monomer ester substituents were chosen as candidates after demonstrating improved solubility of produced lithium alkoxides over the methyl analogue. It was found that straight chain alkyl esters produced polymers, but also resulted in cloudy and insoluble by-products like the methyl ester studied in literature. Even though the branched alkyl esters, (containing the isopropyl and tert-butyl group) produced very soluble alkoxides in THF solution, they were very poor at producing polymers at high conversion and remained relatively unreactive, due to their high pKa’s and steric blocking of the ester carbonyl carbon. The phenyl ester derivatives proved to be the best substituent groups studied, due to their impressive solubility when in the lithium phenoxide form and produced crystal clear solutions post polymerization. Along with solubility, the faster kinetics observed also makes the phenyl esters the monomers of choice to produce soluble CGC polybenzamides in shorter amounts of time. It was also interestingly discovered that the order in phenyl ester reactivity followed the trends understood by aminolysis literature, where the more stable leaving group dominated the kinetics, not the electrophilicity of the carbonyl, which was supported by computation studies.
5.1 Introduction

Chain growth condensation (CGC) polymers are a relatively new class of polymers that have allowed for material scientists to prepare traditional condensation polymers with improved functionalities. CGC also allows for control over molecular weight and end group chemistries and producing polymers with narrow molecular weight distributions. These improvements upon the condensation polymers typically synthesized by industry provides the opportunity for the preparation of polymers and materials that have never before been envisioned, due their controlled nature. The theory behind the CGC process has been extensively reviewed by Yokozawa and coworkers. Typically, the process to create condensation polymers in a chain growth manner, rather than in the conventional step growth process, involves controlling the relative reactivity of the initiator, polymer chain, and monomer, by making the initiator or the growing chain end group more reactive than the monomer’s similar reactive site. This results in preferential addition of the monomer to the initiator or growing polymer chain, rather than monomer reacting with another monomer, and, as a consequence, gives a chain growth mechanism.
More specifically, synthesis of aromatic polyamides using the CGC technique has been studied by various groups spanning almost a decade.\textsuperscript{113, 192, 217} Many techniques have been explored to create the active version of the monomer for the CGC process, including using substituted trimethylsilyl aromatic amines and CsF\textsuperscript{120, 217} to make the nucleophilic amide anion, in addition to employing stronger, non-nucleophilic lithium amide bases\textsuperscript{121, 192} to deprotonate the secondary anilines on the monomer. The proposed theory behind the CGC process involves nucleophilic acyl substitution at the ester substituent end group of the growing chain. Literature suggests that control over the polymerization is achieved when the reactivity of the carbonyl carbon of the ester substituent on the monomer is much less than the reactivity of the ester carbonyl carbon on the initiator or growing chain, causing the growth to mainly occur at the end group of the polymer chain. It is argued that the decrease in reactivity of the monomer’s ester group is obtained when the deprotonated amide anion donates negative charge into the ring, deactivating the para ester substituent by effectively reducing the electrophilicity of the carbonyl carbon. This deactivation argument is primarily explained by the decrease in the electrophilicity of the carbonyl carbon from the shielding nature of the electron rich ring system.

It is well understood in more conventional controlled polymerization techniques (such as controlled radical polymerizations), that control over molecular weight and narrow molecular weight distributions occur when initiation occurs much faster than propagation.\textsuperscript{75} This well understood theory will apply to CGC systems when attempting to obtain optimum control over the polymerization. As such, it is evident that an initiator with a reactive ester group is required when using the CGC method so control can be maintained. This concept was particularly evident in recent work from our group that examined the effect of monomer structure on the kinetics of CGC polymerization (Chapter 4). The results of this work showed that the reactivity of substituted phenyl 4-octylaminobenzoate monomers dramatically increased when the monomer contained an electron withdrawing phenyl ester.
group as the leaving group in the nucleophilic acyl substitution reaction to add monomer
to the polymer end group. However, when polymerizing these reactive monomers, it was
observed that control over the polymerization was decreased when using conventional
initiators for GCG systems. This loss of control was attributed to competition between the
conventionally accepted initiation mechanism for CGC and a self-initiation or self-
condensation process due to the enhanced reactivity of the monomer. Due to the nature
of the conditions used in the CGC polymerization to produce polymer brushes, unlike
controlled radical polymerization techniques, the solution lacks a sacrificial initiator and
consists strictly of deprotonated monomer. Despite this, it was found that polymer formed
in solution during the course of polymer brush formation from the substrate, which was
attributed to self-condensation of the deprotonated monomer.

The theory behind the CGC process shows that monomer self-initiation is not ideal as
it allows for initiation to occur over the course of the polymerization and, as such, produces
polymers with broad molecular weight distributions with unplanned molecular weights. The
concept of self-initiation in substituent effect CGC has not been studied extensively, except
for one study where self-condensation was investigated by employing a premade self-
condensed dimer as an initiator using the CsF activation method. Results of this study
show that dimers do in fact behave like initiators (or growing polymer chains) due to the
amide linkage between the monomers not reducing the reactivity of the ester group despite
the presence of a deprotonated amine. As such, the production of dimers is not ideal,
especially in systems containing a specific initiator, and this process could be a plausible
mechanism for describing the self-initiation observed in the preparation of polymer brushes
or when using very reactive monomers. However, the vast majority of literature on CGC
polymerizations claims that the deprotonated monomer is completely deactivated,
suggesting that no reaction should occur between deprotonated monomers and no self-
condensation or self-initiation should take place. The work presented in this study
investigates how monomers with more reactive ester substituents do not follow the accepted theory. To examine this phenomena, three substituted 4-octylaminobenzoate monomers, with different ester leaving groups, were synthesized and exposed to CGC polymerization conditions without the addition of an initiator. Different bases were also used to investigate the effect of basicity on the polymerization to determine if true deactivation was possible. In addition, a series of initiators with different ester leaving groups were also synthesized to investigate the effect of the initiator activity on control over the polymerization.

5.2 Experimental Section

5.2.1 Materials

Lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS, 1.0 M) in tetrahydrofuran (THF), lithium diisopropylamide (LDA, 1.0 M, THF), dimethylamine solution (2 M, THF), triethylamine (>99.5%), thionyl chloride (SOCl₂, >99.5%), anhydrous dichloromethane (DCM) (stabilized with 50-150 ppm amylene, >99.8%), octanal (99%), sodium triacetoxyborohydride (97%), 4-(dimethylcarbamoyl)benzoic acid (98%), 4-nitrophenol (99%), p-toluic acid (98%), dimethylformamide (DMF, anhydrous, 99.8%) and MgSO₄ were purchased from Sigma Aldrich. Acetic acid, sodium bicarbonate, sodium hydroxide, and ethyl acetate were purchased from Macron. Ammonium chloride (99.9%) was purchased from Baker Scientific, methyl 4-aminobenzoate (98%) from Alfa Aesar. 4-N,N-dimethylaminopyridine (DMAP, 99%), and dicyclohexylcarbodiimide (DCC, 99%) were purchased from Acros Organics, and 4-methylphenol was purchased from Fluka Analytical. Unless otherwise mentioned, all chemicals were used as received without further purification. THF was purchased from Macron and was purified and dispensed through a PURE SOLV MD-4 solvent purification system (activated alumina, copper catalysts and molecular sieves).
5.2.2. Characterization

$^1$H, $^{13}$C, and $^{19}$F nuclear magnetic resonance (NMR) spectra were obtained on a JEOL-500 S MHz spectrometer. Infrared spectra were recorded on a Thermo Scientific Nicolet iS50 Fourier transform infrared (FTIR) spectrometer using a diamond attenuated total reflectance (ATR) crystal. Number-average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$, PDI) were measured using a Viscotek GPCmax gel-permeation chromatography (GPC) unit (eluent: stabilized tetrahydrofuran (OmniSolv) with a flow rate of 1.0 mL/min using PLgel 5 $\mu$m MIXED-C and MIXED-D columns: molecular weight range 200-2,000,000 and 200-400,000 g/mol (polystyrene equivalent), respectively). A calculated $dn/dc$ value of 0.156 was determined and used during the analysis.

5.2.3 Synthesis Methods

5.2.3.1 Synthesis of Monomers and Initiators

_Synthesis of N-octyl Monomers_

The following is a representative procedure used for N-alkylation of the various 4-aminobenzoate esters. The alkylation procedure was adopted from literature$^{192}$ and proves to be very successful for the N-alkylation of the three monomers of interest (Scheme 5.1). To reduce the length of the chapter, the synthesis of the corresponding 4-aminobenzoate precursors mentioned below is highlighted in Appendix C.

![Scheme 5.1. Alkylation procedure used to synthesize monomers with varying ester groups.](image-url)
Methyl 4-(octylamino)benzoate (M-OAB)

Synthesis adapted from literature: methyl 4-aminobenzoate (6.0 g, 38.9 mmol), octanal (5 g, 38.9 mmol), acetic acid (2.9 mL, 51.3 mmol), and sodium triacetoxyborohydride (9.89 g, 46.7 mmol). Product: as white crystals; m.p. 89-90 °C, (8.3 g, yield 81%). ¹H NMR (500 MHz, CDCl₃, δ): 7.85 (d, J = 8.9 Hz, 2H, ArH), 6.54 (d, J = 8.9 Hz, 2H, ArH), 4.13 (br, 1H), 3.83 (s, 3H), 3.14 (t, J = 7.4 Hz, 2H), 1.62 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3376 (Ar-NH-R), 2946, 2920, 2849 (C-H), 1678 (O-C=O), 1569, 1430, 1190, 1105, 832 cm⁻¹.

Phenyl 4-(octylamino)benzoate (P-OAB)

Phenyl 4-aminobenzoate (6.0 g, 28.3 mmol), octanal (3.62 g, 28.3 mmol), acetic acid (2.4 mL, 42.4 mmol), and sodium triacetoxyborohydride (7.8 g, 36.8 mmol). Product: as white crystals; m.p. 112-113 °C, (7.3 g, yield 79%). ¹H NMR (500 MHz, CDCl₃, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.4 (t, J = 8.1 Hz, 2H, ArH), 7.25 (t, J = 8.1 Hz, 1H, ArH), 7.18 (d, J = 8.1 Hz, 2H, ArH), 6.59 (d, J = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3380 (Ar-NH-R), 2921, 2852 (C-H), 1691 (O-C=O), 1594, 1275, 1163, 1075, 742 cm⁻¹.

Trifluoromethylphenyl 4-(octylamino)benzoate (TFMP-OAB)

Trifluoromethylphenyl 4-aminobenzoate (5.0 g, 17.8 mmol), octanal (2.3 g, 17.8 mmol), acetic acid (1.5 mL, 26.7 mmol), and sodium triacetoxyborohydride (4.9 g, 23.1 mmol). Product: as white crystals; m.p. 129-130 °C, (4.9 g, yield 70%). ¹H NMR (500 MHz, CDCl₃, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.7 (d, J = 8.9 Hz, 2H, ArH), 7.3 (d, J = 8.9 Hz, 2H, ArH), 6.59 (d, J = 8.9 Hz, 2H, ArH), 4.25 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q,
$J = 7.4 \text{ Hz, 2H}$, $1.42-1.22 \text{ (m, 10H)}$, $0.88 \text{ (t, } J = 7.4 \text{ Hz, 3H)}$. $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 164.9, 152.9, 132.5, 126.7 (q, $J = 3.8$ Hz) (C-F), 122.5, 116.2, 111.5, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0. $^{19}$F NMR 1 peak; FTIR (ATR): ν = 3376 (Ar-NH-R), 2952, 2924, 2854 (C-H), 1698 (O-C=O), 1598, 1320, 1272, 1159, 1120, 1058, 833, 761 cm$^{-1}$.

**Synthesis of Substituted Initiators**

![Scheme 5.2](image.png)

Scheme 5.2. Synthesis of functionalized phenyl ester dimethyl amide initiators using DCC/DMAP.

**Methyl 4-(dimethylcarbamoyl)benzoate (DMA-M)**

A solution of dimethylamine (4 mL, 8 mmol), triethylamine (0.87 mL, 6.3 mmol), and anhydrous DCM (15 mL) was prepared and added to a solution of the acid chloride (methyl 4-(chlorocarbonyl)benzoate) (1.13 g, 5.7 mmol) (prepared by refluxing 4-(methoxycarbonyl)benzoic acid (1.03 g, 5.7 mmol) in SOCl$_2$ for 2 h, and removing excess SOCl$_2$) in anhydrous DCM (5 mL). The solution was refluxed for 1 h followed by concentration in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel (pentane/ethyl acetate 1:1). Product: off yellow solid. m.p. 108-109 °C; (1.1 g, yield: 91%). $^1$H NMR (500 MHz, CDCl$_3$, 25°C): δ = 8.06 (d, $J = 8.32$ Hz, 2H), 7.47 (d, $J = 8.32$ Hz, 2H), 3.92 (s, 3H), 3.11 (br, 3H), 2.94 (br, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) 170.5, 166.5, 140.7, 131.0, 129.7, 127.2, 52.4, 39.4, 35.3 ppm; FTIR (ATR): 2951, 2853, 1721, 1618, 1277, 1257, 1109, 1078, 726 cm$^{-1}$. 

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Phenyl 4-(dimethylcarbamoyl)benzoate (DMA-P)

In a 100 mL round bottom flask fit with a stir bar was placed 4-(phenoxy carbonyl)benzoic acid (1.1 g, 4.5 mmol) and SOCl₂ (11 mL, 150 mmol). The mixture was refluxed until the acid dissolved, producing the acid chloride. Excess SOCl₂ was removed under vacuum. The remaining acid chloride was dissolved in anhydrous DCM (30 mL). A solution of dimethylamine (2M in THF) (2.73 mL, 5.5 mmol), triethylamine (0.7 mL, 5.0 mmol), and DCM (20 mL) was prepared and added slowly to the acid chloride. The mixture was refluxed for 1 h. The solvent was then removed under vacuum, the residue was dissolved in ethyl acetate and passed through a short column (eluted with ethyl acetate). After removal of the solvent and drying under vacuum, no further purification was necessary. Product: as white crystals; m.p. 111-112 °C, (0.86 g, yield 70%).

1H NMR (500 MHz, CDCl₃, δ): 8.2 (d, J = 8.1 Hz, 2H, ArH), 7.54 (d, J = 8.2 Hz, 2H, ArH), 7.42 (t, J = 8.0 Hz, 2H, ArH), 7.27 (t, J = 8.0 Hz, 1H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH), 3.1, (s, 3H) 2.97 (s, 3H) (N-CH3); 13C NMR (150 MHz, CDCl₃, δ): 170.5, 164.6, 150.9, 141.4, 130.46, 130.40, 129.6, 127.3, 126.1, 121.7, 39.4, 35.4; FTIR (ATR): ν = 3085, 2920, 1724 (O-C=O), 1616 (N-C=O), 1393, 1265, 1085, 876, 720 cm⁻¹.

4-Nitrophenyl 4-(dimethylcarbamoyl)benzoate (DMA-NP)

4-(Dimethylcarbamoyl)benzoic acid (1.63 g, 8.44 mmol) was added to anhydrous DMF (40 mL) in a round bottom flask fit with a stir bar. 4-Nitrophenol (1.17 g, 8.44 mmol) and DMAP (0.060 g, 0.5 mmol) was then added and dissolved. DCC (1.74 g, 8.44 mmol) was then added slowly. The resulting solution was allowed to stir overnight. The urea by-product was removed using vacuum filtration and solvent was then removed under vacuum. The resulting paste was then dissolved in chloroform and ran through a short silica column. The solvent was removed once more and the resulting product was recrystallized from methanol. Product: as white crystals; m.p. 166-167 °C, (1.78 g, yield 67%).

1H NMR (500 MHz, CDCl₃, δ): 8.32 (d, J = 8.1 Hz, 2H, ArH), 8.23 (d, J = 8.1 Hz, 2H, ArH), 7.57 (d, J = 8.0 Hz, 2H, ArH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 3.1, (s, 3H) 2.97 (s, 3H) (N-CH₃).
3.1, (s, 3H) 2.97 (s, 3H) (N-CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$, δ): 170.2, 163.6, 155.5, 145.6, 142.1, 130.6, 129.4, 127.5, 125.4, 122.7, 39.48, 35.4; FTIR (ATR): $\nu$ = 3064, 2930, 1731 (O-C=O), 1610 (N=C=O), 1522, 1397, 1211, 1085, 887, 737 cm$^{-1}$.

4-Methoxyphenyl 4-(dimethylcarbamoyl)benzoate (DMA-MP)

4-(Dimethylcarbamoyl)benzoic acid (2.03 g, 10.51 mmol) was added to anhydrous DMF (50 mL) in a round bottom flask fit with a stir bar. 4-Methoxyphenol (1.31 g, 10.51 mmol) and DMAP (0.060 g, 0.5 mmol) was then added and dissolved. DCC (2.17 g, 10.51 mmol) was subsequently added slowly. The resulting solution was allowed to stir overnight. The urea by product was removed using vacuum filtration and solvent was then removed under vacuum. The resulting paste was then dissolved in chloroform and ran through a short silica column. The solvent was removed once more and the resulting product was recrystallized from methanol. Product: as white crystals; m.p. 131-132 °C, (2.43 g, yield 77%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.2 (d, $J$ = 8.1 Hz, 2H, ArH), 7.54 (d, $J$ = 8.2 Hz, 2H, ArH), 7.12 (d, $J$ = 8.1 Hz, 2H, ArH), 6.95 (d, $J$ = 8.1 Hz, 2H, ArH), 3.65, (s, 3H) 3.16 (s, 3H), 2.95 (s, 3H, N-CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$, δ): 170.5, 165.0, 150.9, 157.5, 144.3, 141.3, 130.6, 130.3, 127.2, 122.5, 114.6, 55.7, 35.4; FTIR (ATR): $\nu$ = 2834, 1728 (O-C=O), 1620 (N=C=O), 1620, 1504, 1392, 1262, 1201, 1071, 1034, 1071, 737, 662, 528 cm$^{-1}$.

Phenyl 4-(dimethylamino)benzoate (AB-P)

4-(Dimethylamino)benzoic acid (3.0 g, 18.16 mmol) was added to anhydrous DMF (40 mL) in a round bottom flask fit with a stir bar. Phenol (1.71 g, 18.16 mmol) and DMAP (0.11 g, 0.91 mmol) was then added and dissolved. DCC (3.75 g, 18.16 mmol) was subsequently added slowly. The resulting solution was allowed to stir overnight. The urea by product was removed using vacuum filtration and solvent was then removed under vacuum. The resulting paste was then dissolved in chloroform and ran through a short silica column. The solvent was removed once more and the resulting product was recrystallized from methanol. Product: as white crystals; m.p. 178-179 °C, (2.88 g, yield 67%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.06 (d, $J$ = 8.1 Hz, 2H, ArH), 7.40 (t, $J$ = 8.1
Hz, 2H, ArH), 7.23 (t, J = 8.0 Hz, 1H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 3.08, (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.7, 153.7, 151.3, 132.1, 129.4, 125.5, 122.1, 116.1, 110.8, 40.2; FTIR (ATR): $\nu$ = 2930, 1705 (O-C=O), 1594, 1368, 1275, 1066, 825, 760, 696, 486 cm$^{-1}$.

Phenyl 4-methylbenzoate (MB-P)

p-Toluic acid (1.36 g, 10.0 mmol) was added to anhydrous DMF (40 mL) in a round bottom flask fit with a stir bar. Phenol (0.94 g, 10.0 mmol) and DMAP (0.10 g, 0.94 mmol) was then added and dissolved. DCC (2.06 g, 10 mmol) was subsequently added slowly. The resulting solution was allowed to stir overnight. The urea by product was removed using vacuum filtration and solvent was then removed under vacuum. The resulting paste was then dissolved in chloroform and ran through a short silica column. The solvent was removed once more and the resulting product was recrystallized from methanol. Product: as white crystals; m.p. 74-75 °C, (1.67 g, yield 78%). $^1$H NMR (500 MHz, CDCl$_3$,δ): 8.09 (d, J = 8.3 Hz, 2H, ArH), 7.42 (t, J = 8.2 Hz, 2H, ArH), 7.31 (d, J = 8.2 Hz, 2H, ArH), 7.26 (t, J = 8.1 Hz, 1H, ArH), 7.2 (d, J = 8.2 Hz, 2H, ArH), 2.45 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.3, 151.1, 144.4, 130.3, 129.5, 129.4, 126.9, 125.8, 121.9, 21.9; FTIR (ATR): $\nu$ = 3308, 2924, 2850, 1720 (O-C=O), 1268, 1190, 1079, 743, 686 cm$^{-1}$.

5.2.3.2 Polymerization Methods

Polymerization Employing no Initiator and LiHMDS Base

A typical polymerization procedure where no initiator was used is depicted in Scheme 5.3. The reaction was conducted by placing 0.5 mmol of a given monomer (0.13 g M-OAB, 0.162 g P-OAB, or 0.195 g TFMP-OAB) in a 25 mL round bottom flask with a stir bar. The flask was capped with a septum and purged with argon. Anhydrous THF (10 mL for 1 equivalent of base experiments or 5 mL for 10 equivalents of base) was then injected into the flask containing the monomer and the solution was brought to the temperature of interest using a cooling bath. LiHMDS (0.6 mL, 0.6 mmol for 1 equivalent of base or 5 mL, 5 mmol for 10 equivalents of base) was then injected, thus starting the reaction. Aliquots were removed and quenched, by injecting into a saturated ammonium chloride solution, during the course of the polymerization. The
resulting polymer was isolated via extraction with DCM, washed with aqueous 1 M NaOH, dried under magnesium sulfate, and isolated by removing the solvent and other by-products under vacuum, followed by further drying in a vacuum oven at 60 °C for 2 h.

Scheme 5.3. Reaction employing no initiator and different equivalents of base.

Due to the high reactivity of the trifluoromethylphenyl monomer, the two temperatures of interest were -48 °C (achieved using dry ice and acetonitrile) and -20 °C (brine ice bath). The lower reactivity of the phenyl and methyl moiety resulted in the experiments being conducted at -20 °C and 0 °C.

Polymerizations Employing LDA Base

A typical polymerization procedure utilizing the MB-P initiator, the monomer of interest, and LDA as the base is depicted in Scheme 5.4. The reactions were conducted by placing 0.5 mmol of a given monomer (0.13 g M-OAB, 0.162 g P-OAB, 0.195 g TFMP-OAB) and the initiator, phenyl 4-methylbenzoate (MB-P) (0.0021 g, 0.01 mmol), in a 25 mL round bottom flask with a stir bar. The flask was capped with a septum and purged with argon. Anhydrous THF (10
mL) was then injected into the flask and the solution was brought to -20 °C. LDA (0.5 mL, 0.5 mmol), was the injected into the solution, thus starting the reaction.

Scheme 5.4. Polymerization employing MB-P initiator and LDA base for the three monomers studied.

The reaction containing the methyl ester monomer (M-OAB) was warmed to room temperature (20 °C) after addition of the LDA, while for the remaining monomers (P-OAB and TFMP-OAB) the reaction was kept at -20 °C. After 6 h, the solutions were then poured into a stirring saturated ammonium chloride solution. The resulting polymer was isolated via extraction with DCM, washed with aqueous 1 M NaOH, dried under magnesium sulfate and isolated by removing the solvent and by-products under vacuum, followed by further drying in a vacuum oven at 60 °C for 2 h.

Polymerization Employing Various Initiators

A typical polymerization procedure utilizing the desired initiator and the monomer of interest is depicted in Scheme 5.5. 0.5 mmol of a given monomer (0.13 g M-OAB, 0.162 g P-OAB, 0.195 g TFMP-OAB) and 0.01 mmol of the desired initiator (2.4 mg AB-P, 2.1 mg MB-P, 3.1 mg DMA-NP, 3.0 mg DMA-MP, 10.4 mg DMA-M, 2.7 mg DMA-P) was placed in a 25 mL
round bottom flask with a stir bar. The flask was capped with a septum and purged with argon. Anhydrous THF (10 mL) was then injected into the flask and the solution was brought to the temperature of interest using a cooling bath. LiHMDS (0.6 mL, 0.6 mmol) was injected into the solution, thus starting the reaction.

Scheme 5.5. Polymerizations employing initiators with various substituents for the more reactive monomers studied.

After 2 h, the solution was poured into a stirring saturated ammonium chloride solution. The resulting polymer was isolated via extraction with DCM, washed with aqueous 1M sodium hydroxide to remove phenol byproducts, dried under magnesium sulfate and was isolated by removing the solvent and by-products under vacuum, followed by further drying in a vacuum oven at 60 °C for 2 h.

5.2.3.3 Computation Modeling Parameters

All computations used the high-performance computing facility accessible through the Colorado School of Mines campus. The Gaussian 09 package was utilized for all calculations performed during this study. Geometry and transition state optimizations were performed using the 2006 version of the Global hybrid Minnesota functional (M06-2X) and the split valance
polarized basis set 6-31G(d). The transition states were confirmed with frequency calculations with the force constants computed at the first point and with suppression of the Eigen test. The charge of each atom was calculated using a Natural Bond Orbital (NBO) analysis. Implicit solvation of THF was incorporated into the calculations using the integral equation formalism variant polarizable continuum mode (IEFPCM). HOMO and LUMO plots were generated on the basis of calculating the areas of electron density at the highest occupied and lowest unoccupied molecular orbitals. Activation energies and reaction rates for the polymer growth mechanism were gained from implementing the KisTheLP package.

5.3 Results and Discussion

Synthesis of Initiators

The initiators chosen for this study consist of the previously reported activated electron withdrawing dimethyl amide group (used to mimic the attachment to surfaces through the aminopropylsilane functionality), along with an electron donating dimethyl amine group and a more neutral methyl group. As a main focus of this chapter is to investigate the effect of the initiator ester substituent group on the polymerization of various reactive monomers. Based on the previous monomer studies (Chapter 4), it has been demonstrated that the nature monomer ester group has a large impact on the reactivity of the ester toward CGC, due to the stability of the leaving group and the electrophilicity of the esters carbonyl carbon. As mentioned previously, the initiator reactivity is very important due to the ratio of the relative rates of initiation to propagation and it’s important in producing polymers with narrow molecular weight distributions. In addition, in systems where self-initiation is present, it is important that the initiation of chains using a fixed initiator is the dominant process, otherwise, once again, broad molecular weight distributions will result. The first two initiators utilized in this study have the methyl and phenyl ester derivatives and were prepared using a procedure previously reported in literature.
A different synthesis scheme was utilized for the synthesis of the substituted phenyl ester dimethyl amide initiators (Scheme 5.2). The synthesis of these initiators was completed by first making the dimethyl amide benzoic acid precursor and coupling it with the desired substituted phenol. The synthesis scheme and detailed procedures for the precursors can be found in Appendix C.

5.3.1 Effect of No Initiator and Different Molar Equivalent of LiHMDS to Monomer on CGC Self-Initiation via Monomer Condensation

The CGC process has revolutionized the synthesis of polymers typically prepared by conventional step growth processes by allowing for the formation of these polymers with controlled molecular weights, a narrow molecular weight distribution, improved functionality, and more complex architectures. Previous work in Chapter 4 has demonstrated that well-defined aramids can be produced using the CGC method with various phenyl 4-octylaminobenzoate monomers, a non-nucleophilic lithium amide base to prepare the amide anion on the monomer, and an initiating species containing an activated ester. Literature has also shown a preference towards methyl ester based monomers for substituent effect CGC, as these monomers yield low-boiling point methanol as the by-product, after the aqueous workup, which is claimed to make the overall process more convenient.\textsuperscript{192} However, previous work by our group utilizing the methyl ester monomer M-OAB to produce polymer brushes from surface immobilized initiators demonstrated that even though polymer brushes could be formed, issues with by-product solubility and slow kinetics restricted the thickness of the polymer brushes (Chapter 3).\textsuperscript{6} In an effort to better understand the effect of monomer structure on the kinetics of the CGC process and on the polymers produced, we recently investigated the polymerization of a variety of N-octyl benzamide based monomers with different ester substituents. The main conclusion from this work was that the structure of the monomers ester leaving group dictates the reactivity of the monomer in CGC and the solubility of the polymerization by-products (Chapter 4). One of the most
interesting observations from this previous study was that while the phenyl esters monomers demonstrated faster reactivity and increased solubility of the lithium phenoxide by-products, they were also more difficult to control during the polymerization, which resulted in broader molecular weight distributions and multi-modal GPC traces. This loss of control was attributed to competition between the conventionally accepted initiation mechanism for CGC and a self-initiation or self-condensation process due to the enhanced reactivity of the monomer.

Despite the dramatic effect that self-initiation can have on the CGC process, to the best of our knowledge, there are no detailed studies of this process and, in fact, there is only one previous paper that considers self-initiation in CGC, however, that paper only investigates dimer-based initiation in a system with CsF activation.\textsuperscript{218} In an effort to understand the self-initiation process in CGC, three different N-octyl benzamide based monomers, with different ester substituents and of varying activity, were exposed to polymerization conditions without the presence of initiator and with different molar equivalents of the base LiHMDS. The methyl ester monomer M-OAB was chosen as a control, since it has been utilized in previous studies.\textsuperscript{6} The polymerization attempt of M-OAB with no initiator and 1 molar equivalent of LiHMDS yielded no conversion over a 12 h period at either 0°C or -20°C, indicating that these temperatures are sufficient to completely deactivate the monomer towards self-initiation or the process is too slow to be observed at these temperatures during the time allowed. This was one of the beneficial aspects of the why methyl ester system was chosen for the brush study.\textsuperscript{6} This is confirmed by previous studies that have demonstrated that the methyl ester monomer has low reactivity at these temperatures, even in the presence of initiator, due to the basicity of the methoxide leaving group (Chapter 4).

Continued experiments studied the self-initiation properties of the two more reactive monomers, P-OAB and TFMP-OAB, at these temperatures as well. Results from these experiments show that polymer forms for both P-OAB and TFMP-OAB monomers when no
initiator is employed. A typical polymerization progression for P-OAB with no initiator at 0°C and TFMP-OAB with no initiator at -20°C is shown in Figure 5.1 using overlaid GPC traces.

![Figure 5.1. GPC traces displaying the progress of reactions employing no initiators using one equivalent of LiHMDS base for two different monomers at different temperatures.](image)

From these traces it is clear that the monomer signal, near a retention volume of 18.5 mL, decreases with time, while the polymer signal moves left, indicating an increasing molecular weight. However, along with the increasing molecular weight, there is also an increase in the molecular weight distribution, indicated by a broadening of the polymer peak.

In addition, the GPC traces for polymerization of the faster TFMP-OAB monomer show a trace with a high molecular weight shoulder, which suggests that polymer chains are being initiated at various stages during the polymerization and are participating in chain-chain reactions that would lead to larger molecular weights. These results suggest that self-initiation not only takes place in the systems with the more reactive P-OAB and TFMP-OAB monomers (due to the formation of polymer when no initiator is added) but it is also occurring over the course of the reaction, resulting in increased PDIs. These visual observations were also confirmed in plots of molecular weight and PDI versus monomer conversion for the polymers prepared from P-OAB and TFMP-OAB (Figure 5.2). The NMR conversion data was obtained using the ratio of the monomer doublet
signal to the broader polymer doublet signal of the aryl protons adjacent to the substituted aniline group for every particular aliquot taken.

Figure 5.2. Average molecular weight ($M_n$) and polydispersity index (PDI) evolution with conversion for polymerizations employing no initiators and DMA-P initiators for phenyl and trifluoromethly (TFMP) monomers at different temperatures.

The gradually increasing trend of molecular weight with conversion for the reactions with no initiator in Figure 5.2 poses an interesting explanation of the behaviour of the system. It is important to notice that the same increasing trend in molecular weight is followed by both reactive monomers, even when they are prepared at vastly different temperatures. This behaviour suggests that the initiation process occurring in all of the reactions is quite similar and there are a few explanations for this trend. The gradual increase in molecular weight with conversion, when compared to controlled chain growth reactions where the observed trend is more linear, means that instead of a fixed amount of polymer chains in the system, the number of chains may be decreasing over the course of the polymerization, resulting in an increasing slope of the molecular weight versus conversion plot. This observation may be a direct result of chains being initiated by the self-initiation process. When a chain is initiated in the self-initiation reaction, one chain end will consist of a deprotonated, or possibly protonated, amine. These reactive chains ends are capable of reacting with the active ester group of another polymer, thus increasing the overall
molecular weight and overall distribution of chains of the reaction while also decreasing the total number of chains present.

The data displayed in the PDI correlation with conversion tend to show opposite trends for both monomers. This difference in PDI trends, specifically with the unusual decreasing PDI in the -50°C TFMP/no initiator system could be due to the slow self-initiation, which would then follow a conventional chain growth process. Either way, the results presented in Figure 5.2 suggest that further studies should be conducted to understand the behaviour of these systems.

To further investigate the behaviour of these monomers, the kinetics of the polymerization were examined using semi-logarithmic plots of conversion versus time at various temperatures, base concentrations, and for reactions with and without added initiator (Figure 5.3). These plots show that in each case there appears to be a linear first order relationship, however, the slope of the plots differ showing different rates of reaction. It is evident in this figure that for both monomers at all temperatures when using an initiator the reaction proceeds with the fastest kinetics. When no initiator is employed for all of the monomers and temperatures with one equivalent of base, the kinetics are reduced by one order of magnitude. Even though the use of an initiator is shown to increase the overall rate of polymerization and the kinetics of self-initiated polymerization still occurs at an appreciable rate, suggesting that self-initiation is an inherent process occurring with faster monomers. From this data and the knowledge of the reaction propagation constants (reported in Chapter 4), the effective “initiator” concentrations were back calculated. The results of these calculations were included in Figure 5.3. It is reasonable to assume that the rate constant for propagation is the same for all polymerizations of a particular monomer at a particular temperature, as the propagation reaction (after multiple monomer additions) should be independent of the initiating species. This assumption allows for calculation of the effective initiator concentration in the cases where no initiator was added. In the cases where there is a known initiator concentration, $10^{-3}$ M in each case, the semi-logarithmic plots shows the fastest
overall kinetics. From the semi-logarithmic plots when there is no initiator added, the plots show the calculated effective initiator concentrations and, in general, all are approximately one order of magnitude smaller than the added initiator, which would result in slower kinetics for the same propagation constant. A particularly interesting observation with the calculated effective initiator concentrations is how similar they are regardless of monomer type or temperature. This suggests that the process of self-initiation is independent of monomer structure and temperature and possibly dependent on the common factor between each system, the LiHMDS. From this data, it is evident that the initiator is effective at controlling the polymerization by increasing the reaction kinetics, and thus consuming monomer before it can self-condense with one another due to the more linear and smaller sloping trends that the polymerizations employing the DMA-P initiator provide (Figure 5.2).

Figure 5.3. Kinetic data relating the use of \([I]_0 = 0.001\) M DMA-P initiator to control the reaction and reactions employing no initiator with 1 equivalent and 10 equivalent of base for 3 different temperatures and the two fast monomers of interest.
One way envisioned to inhibit the self-initiation observed in the results with addition of 1 equivalent of base is to use an excess of the base, LiHMDS. Assuming the self-initiation reaction is favoured by reaction between a protonated monomer and a deprotonated monomer, the addition of an excess amount of base will ensure the equilibrium of the monomer deprotonation reactions is shifted towards complete deprotonated of the monomer, which would decrease the amount of the more reactive protonated monomer present for self-initiation to occur. This notion was investigated by performing the same experiments as above, at -20 °C for the TFMP-OAB monomer and 0 °C for the P-OAB monomer, with the addition of 10 equivalents of base to monomer compared to the one equivalent used in the above studies and in the vast majority of literature studies (Figure 5.3). These temperatures were chosen as polymerizations run with 10 equivalents of base at lower temperatures for each monomer were extremely slow. The semi-logarithmic plots of conversion versus time do demonstrate that addition of excess base does, indeed, slow the self-initiated polymerization kinetics (as evidenced by the decreasing slope) by almost two orders of magnitude, but importantly it does not completely stop the self-initiation reaction from occurring as polymer was still formed. Using the procedure outlined previously, the effective initiator concentration for these systems were also calculated and are shown to be approximately two orders of magnitude smaller than the reaction employing using an initiator and one order of magnitude lower than when one equivalent of base is used. Once again, it is interesting to note that the calculated effective initiator concentration, while lower than the values at one equivalent of base, also appear to be somewhat independent of monomer structure and temperature. The primary consequence of these studies is that as self-initiation appears to occur in all systems regardless of monomer type, in order to maintain control over the polymerization it is important to use an initiator that dominates so the majority of monomer is consumed before large amounts of self-initiation can occur.
5.3.2 Employing a Stronger LDA Base

The main reason why self-initiation was thought to be occurring was that there is possibly a low concentration of protonated monomer available for the dimerization reaction in the solution. One of the reasons that there would be protonated monomer available is that the base employed, lithium hexamethyldisilazide (LiHMDS), is not basic enough to deprotonate all of the monomer, due to the similar pKa’s of the monomer and the LiHMDS base (both having a pKa ~ 26).\(^{219}\) This would result in an equilibrium concentration of protonated monomer present in solution. This issue addressed in this study by using a stronger base, namely lithium diisopropylamide (LDA). Like LiHMDS, LDA is considered to be a non-nucleophilic base and it is extensively used in enolate chemistry, due to its non-nucleophilic nature towards esters.

The use of LDA as a base for CGC to produce aramids has been examined previously for the methyl and ethyl ester monomer systems.\(^{116, 192, 210}\) However, the two papers citing the use of LDA for CGC reported mixed results. Yokozawa et al. claims that LDA is too nucleophilic for the methyl ester monomer and, as a result, the diisopropyl amide replaces the ester of the initiator and/or the monomer, making them unreactive towards CGC and resulting in no polymer formation;\(^{192}\) whereas, Sugi and Ohishi observed that CGC of the meta substituted methyl ester monomer using LDA presents resulted in the formation of polymer.\(^{116, 210}\) Although, Sugi and Ohishi also reported that there was a limiting conversion in the meta monomer system that limited the amount of polymer formed and cited Yokozawa’s work when proposing that the limiting conversion is caused by the replacement of the end group with an inactive dimethylamide during the reaction. Despite this common conclusion regarding end group replacement when LDA is used as the base, it is important to note that neither group provided evidence to support this claim. As a result of the conflicting literature regarding the use of LDA as a base for substituent effect CGC,
we decided to re-examine the use of the much stronger base, LDA (pKa = 36), as a candidate for the CGC of various ester based monomers used above, with the hypothesis that it is the basicity of LDA that affects the reaction, not the nucleophilicity.

*LDA with MB-P Initiator*

CGC polymerizations were conducted using the monomers M-OAB, P-OAB and TFMP-OAB, LDA as the base, and the initiator MB-P (Scheme 5.4). To ensure the purity of the LDA it was titrated using diphenyl acetic acid to establish the accurate concentration each time before it was used. A polymerization time of 6 h was used for TFMP-OAB and P-OAB at -20 °C and M-OAB at 20°C, and in each case polymer was formed. The molecular weight, PDI, and conversions data for the polymerizations was determined by NMR and GPC and is listed in Table 5.1. In each case, the NMR spectra for the produced polymer resembled that for the polymer made using LiHMDS base. However, in each case the polymerizations with LDA did not reach 100% conversion, as is usually observed when LiHMDS is used as the base, agreeing with literature results for polymerization of the meta monomer using LDA. The lower conversion is also evident from the GPC traces, with a monomer peak appearing at the typical 18.5 mL retention time (see Appendix C). With a theoretical molecular weight of 11,500 g/mol for a poly(N-octyl)benzamide with a DP of 50, the very close molecular weights presented in Table 5.1, along with the narrow molecular weight distributions that the polymers grown using LDA with the MB-P initiator assemble in a chain growth manner.

Table 5.1. Polymerization results when LDA base was employed for the CGC polymerization of the various monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Conversion (%)</th>
<th>Theoretical $M_n$ (g/mol)</th>
<th>$M_n$ (NMR) (g/mol)</th>
<th>$M_n$ (GPC) (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-OAB</td>
<td>80</td>
<td>9,200</td>
<td>9,240</td>
<td>5,260</td>
<td>1.08</td>
</tr>
<tr>
<td>P-OAB</td>
<td>93</td>
<td>10,700</td>
<td>10,740</td>
<td>10,360</td>
<td>1.11</td>
</tr>
<tr>
<td>TFMP-OAB</td>
<td>97</td>
<td>11,150</td>
<td>11,210</td>
<td>13,380</td>
<td>1.16</td>
</tr>
</tbody>
</table>
These results refute previous literature examining the CGC of M-OAB with LDA, as polymer was obtained in our case, and agree with results presented in the paper examining the meta monomer, in that we observed a limiting conversion. To further investigate the reason for a limiting conversion in the CGC systems with LDA, NMR was used to examine the end groups of both the polymer and unreacted monomer. In each case, the NMR spectra of the polymerizations indicate that methyl ester end groups of both the unreacted monomer and resulting polymer are visible. As such, in contradiction to the previously published papers, it appears as though rather than LDA replacing the ester end group, it is participating in other side reactions, possibly due to the very basic nature of LDA. For example, there is a number of literature reports on the use of LDA to lithiate aromatic substrates. These reports show that when the aromatic ring contains an electron withdrawing carbonyl compound or halogenated substituent, addition of LDA results in ortho-lithiation of the ring. These results demonstrate that LDA is a strong enough base to remove aromatic protons, which is an issue to consider for the system studied herein. Each of the monomers used in this study has an ester attached to the aromatic ring, which provides the possibility that a lithiation reaction could be occurring with a fraction of monomer making it unreactive to polymerization. As such, even though we were able to produce polymers with LDA as the base, the presence of side reactions make it not ideal as the base for CGC polymerizations to produce well-defined aramids.

**LDA Base Using No Initiator**

Since it has been demonstrated that polymer can be formed using LDA as the base in the presence of an initiator, it is appropriate to examine the possibility of self-initiation when using LDA. To do this, similar polymerization experiments, as described for the LiHMDS base, were conducted with no initiator and LDA at one equivalent of base. After a reaction time of 6 h, at -20 °C for both the M-OAB and P-OAB monomers no conversion was observed. When observing the NMR spectra, the integrity of the monomers also shows
not to be changed, suggesting that LDA did not replace the ester of the monomers, but rather deprotonated the monomer, and when the reaction was quenched, the monomer would be re-protonated, returning the monomer back to its original state.

The TFMP-OAB monomer, however, did not yield monomer after the time allowed and seemed to produce polymer as a result of the polymerization when examining NMR and appearance of the resulting residue. More studies need to be conducted on this system to further understand the initiation mechanism for this reaction and the nature of the product. Potential explanations for the polymer formed from TFMP-OAB and LDA could be that LDA may be is that TFMP monomer may be reactive enough towards self-condensation even during fully deprotonated conditions at the relatively high temperature of -20°C, allowing for self-initiation and eventual polymerization. Another concept to consider is that the trifluoromethyl group on the phenyl ester is another electron withdrawing group where ortho-lithiation can take place. The NMR spectrum also seemed to be somewhat unrecognizable when comparing intact polymers, perhaps due to the combination of these phenomena.

5.3.3 Proposed Self-Initiation Mechanisms

When examining the results above, it becomes obvious that the possible mechanism for the self-initiation process is complex. The one theory previously proposed involved the presence of some concentration of protonated monomer, depending on the equivalents of base used. This theory focuses on the idea that the higher reactivity of the protonated monomer towards nucleophilic attack, as a result of the lack of the deactivating effect of the amide ion, would act as the sites for self-initiation. If this was the case, the concentration of initiation sites should be dependent on base concentration, which is observed, and using a large excess of base should effectively eliminate self-initiation due to the equilibrium shift, which is not observed. As such, the possibility of other mechanisms requires some discussion.
Scheme 5.6 demonstrates the three reactions that may be involved in the self-initiation process. The first reaction is as described above and involves reaction between a more reactive protonated monomer and the nucleophilic deprotonated monomer, with a reaction constant $k_i$. The produced dimer initiator has an amide bond, which in turn, makes the end ester group more reactive and effectively behaves like a growing polymer chain and continues chain growth propagation. The second reaction is between two deprotonated monomers to produce a deprotonated dimer with a reactive constant of $k_{i(-)}$. Again, in this reaction formation of the dimer creates a molecule that mimics a growing chain and continues propagation. In each case, the dimers are believed to be the initiating species in the reaction, which leads to the addition of monomer with a propagation constant, $k_p$. The number of initiating sites will depend on the rate of formation of dimer and, from the reactions below, if deprotonation reduces the reactivity of the monomer ester group, then $k_i$ should be larger than $k_{i(-)}$.

While the reactions in Scheme 5.6 provide a basis for trying to understand the self-initiation process, they do not effectively describe the experimental results. As described in Chapter 4, the reactivity of monomers to substituent effect CGC is strongly dependent upon the structure of the
leaving group in the nucleophilic acyl substitution reaction. As such, any reaction involving monomers should be dependent on the monomer structure, with the order of reactivity from highest to lowest being TFMP-OAB, P-OAB, and M-OAB. Therefore, it is reasonable to assume that the initiation reactions involving TFMP-OAB should occur at a faster rate and result in differences in the effective initiators and molecular weight in these systems, compared to the other monomers. However, as observed above in Figures 5.2. and 5.3, the molecular weight versus conversion and calculated number of effective initiators appears to be independent of monomer structure.

Another factor to consider when examining potential mechanisms that influence self-condensation is the nature of the deprotonated monomer in solution. When investigating the nature the base being used, literature proposes that the structure of LiHMDS in solution is not as simple as many portray.\textsuperscript{227} The complexity of the solution structure of LiHMDS arise from the presence of the lithium counter ion. The structure of LiHMDS, and other amide bases, in the solid state and in a variety of solvents has been studied extensively and the results of these studies provide clues to possible reaction pathways in the self-initiation reaction. Due to the high Lewis acidity that lithium adopts in the solid state, the structure of LiHMDS conforms to a cyclic trimer, where three molecules are arranged in a cyclic state with alternating Li-N-Li “bonds.”\textsuperscript{228} In THF solution, increased solvation allows for a breakup of the trimer to adopt more of a dimer structure, where THF solvates the exposed lithium, with the most extreme case being a solvated monomer.\textsuperscript{227}

When this understanding is applied to lithiated monomers produced in this study, two potential structures can be proposed (Figure 5.4). Since both the monomer and base employed contain two relatively large substituent groups, the potential to make lithiated dimers remains a possibility. If these structures do, in fact exist, it would vastly change the understanding of the “deactivation” theory, due to the almost covalent character that would keep the negative charge of the nitrogen
from being very delocalized. The lithium species associated with the negative charge on the nitrogen has the opportunity to keep the charge from being delocalized on the benzene ring, keeping the carbonyl from being shielded and becoming less electrophilic. This solvated lithiated monomer or dimer would contain a more reactive carbonyl that could become an initiating site for the polymerization.

![Solvated Dimer and Solvated Monomer](image)

Figure 5.4. Potential structures that reactive monomer could adopt in THF solution, due to the aggregating potential of Lithium with adjacent amide ions.

### 5.3.4 Effect of Initiator Structure on Polymerization Control

As mentioned above, it is important for any controlled chain growth polymerization technique to have fast initiation relative to propagation for the preparation of well-defined polymers with narrow molecular weight distributions. Based on the results above, it is evident that CGC polymerizations occur without added initiators for more reactive monomers and while this reaction appears to happen at different rates, it results in polymers with broader molecular weight distributions. As such, an approach to improve the control over the CGC of these monomers would be to design initiators that have improved reactivity. To examine this hypothesis a series of different initiators for CGC were synthesized with varying substituents in the para positions (Scheme 5.2) and used to polymerize the more reactive monomers P-OAB and TFMP-OAB (Scheme 5.5). The initiator structure was varied with substituents of either electron withdrawing
or donating character and the effect of structure on polymerization control was observed by monitoring the molecular weight properties of the polymers produced (Figure 5.6 and Table 5.2).

The first trend investigated was the effect of the initiator ester leaving group structure on the CGC polymerization (Chapter 4). To examine this, the same initiator backbone used in previous literature (4-dimethylamide) was employed with the leaving group altered by varying the electron donating or withdrawing character attached to a phenyl ring. The second series of experiments performed kept the phenyl leaving group the same while varying the inductive effect of the substituent group at the para position of aromatic initiator. The groups of interest again range from the previously used electron withdrawing dimethylamide functionality to a more electron donating dimethylamine moiety. The methyl ester initiator employed in literature for the methyl ester monomer system (DMA-M) is also examined despite the poor reactivity of the methyl ester group.

The initiation effectiveness was determined by the broadness and location of the GPC traces. The most controlled polymer obtained would show the narrowest trace, with a PDI approaching 1.0, due to swift initiation relative to propagation and the least controlled polymer would yield a higher molecular weight polymer with a broad molecular weight distribution, due to the competing self-initiation and subsequent propagation reactions. If the self-condensation reactions produced an initiators with a lower concentration than the unreactive planned initiator, the reaction would result in higher molecular weight polymers, due to the higher ratio of monomer to initiator in the system.

As predicted, the qualitative results presented in the overlaid GPC traces for both the P-OAB and TFMP-OAB monomers with varying initiators show that all of the phenyl initiators achieve some level of control over the polymerization when compared to self-initiated reactions (Figure 5.6). A more quantitative set of data acquired from analysing the GPC traces can be viewed in Table 5.2, where the PDI and $M_n$ values are listed. Figure 5.6 for both monomers shows that all initiators containing a phenyl ester except the dimethyl amino version (AB-P) yields lower
molecular weight polymers with narrower distributions. The remaining traces, initiators that contain the methyl ester (DMA-M) dimethyl amino (AB-P) and polymer formed with no initiator give similar traces for the TFMP-OAB monomer with higher molecular weight polymers with broader distributions. The traces in Figure 5.6 show that the more reactive initiators produce polymers with narrower molecular weight distributions and with a lower amount of a higher molecular weight shoulder. While most polymerizations were conducted at -20 °C, the relatively high PDI values for TFMP at this temperature (PDI = 1.2) were indications that the control was not optimal at this temperature, so an experiment using DMA-NP as an initiator was conducted at -50 °C to see if a narrower molecular weight distribution was possible. The results from this experiment is included in Figure 5.6 and Table 5.2, and does show that a narrower distribution was achieved, suggesting that colder temperatures are required for the more reactive monomer.

Similar behaviour is observed for the phenyl ester monomer (P-OAB), where the AB-P initiator is demonstrated to be the worst initiator chose, with the largest molecular weight with the largest PDI. Since no appreciable polymer forms with no initiator or reactions employing DMA-M at -20°C, the results are omitted from the GPC traces because less than complete conversion was achieved after the 2 h allotted.

![Figure 5.5. GPC traces resulting from polymers formed using candidate initiators using both monomers at the same temperature.](image)
Table 5.2. Compilation of number average molecular weights ($M_n$) and polydispersity index (PDI) for phenyl and TFMP monomers with various initiators at -20 °C at 100% conversion. Theoretical $M_n$ values are 11,500 g/mol for planned degree of polymerization of 50.

<table>
<thead>
<tr>
<th></th>
<th>PDI (GPC)</th>
<th>$M_n$ (GPC) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenyl</td>
<td>TFMP</td>
</tr>
<tr>
<td></td>
<td>Phenyl</td>
<td>TFMP</td>
</tr>
<tr>
<td>DMA-NP (-50°C)</td>
<td>1.08</td>
<td>-</td>
</tr>
<tr>
<td>DMA-NP</td>
<td>1.17</td>
<td>1.2</td>
</tr>
<tr>
<td>DMA-P</td>
<td>1.16</td>
<td>1.19</td>
</tr>
<tr>
<td>DMA-MP</td>
<td>1.17</td>
<td>1.27</td>
</tr>
<tr>
<td>MB-P</td>
<td>1.2</td>
<td>1.27</td>
</tr>
<tr>
<td>AB-P</td>
<td>1.42</td>
<td>1.67</td>
</tr>
<tr>
<td>DMA-M</td>
<td>-</td>
<td>1.63</td>
</tr>
<tr>
<td>No Initiator &amp; 1eq. Base</td>
<td>-</td>
<td>1.75</td>
</tr>
</tbody>
</table>

It was interesting to note that the DMA-M initiator did allow for higher conversion allowing for only 65% compared to the reaction with no initiator which reached 25% conversion, suggesting that the initiator may be more reactive than self-condensation of deprotonated monomers.

It is proposed that the higher molecular weight shoulders are due to the self-initiated oligomers/polymer chains attaching to other propagating chains to produce a higher molecular weight polymer than originally planned. The trend observed is straightforward and follow the trends reported in literature, where the more stable the leaving phenoxyde (electron withdrawing substituent), the faster the reaction. This means the faster initiator should be the p-nitrophenoxide analogue (DMA-NP), compared to the expected slower initiating of the methyl ester group (DMA-M) (Figure 5.7).

The least performing initiators chosen for this study were the extremes for both cases being the dimethylamino substituent (AB-P) and the methyl ester, (DMA-M). The inductive effect can be used to explain the poor performance and has a similar explanation to the behaviour of deprotonated monomers by effectively decreasing the reactivity of the ester carbonyl. The methyl ester initiator’s (DMA-M) poor performance is due to the understood poor reactivity of methyl
esters, even with the electron withdrawing dimethylamide functionality on the initiator. Both initiators produced polymers that resemble polymers that were produced using no initiators for the TFMP monomer suggesting that they are ineffective at starting the polymerization before self-initiation can occur.

Figure 5.6. Reactivity trends observed for studied initiators. The most reactive initiator is expected to contain electron withdrawing groups on both the initiator and leaving phenyl ester group, DMA-NP.

5.3.5 Computation

*Charges Reflecting Electrophilicity of the Carbonyl*

In attempt to further understand the behaviour observed in the results above, computation was used to examine the observed the trends. The study conducted was to examine the electrophilicity of the various carbonyls participating in the reactions, similar to that performed in Chapter 4. When examining the initiators, the trend that is observed is that the most reactive initiator has the electrophilic carbon that is part of the reacting ester carbonyl group. When examining the effect of the substituent on the initiator, there is a trend in atomic charges on the carbon of the carbonyl that is expected (Table 5.3). The more electron withdrawing dimethylamide group in DMA-P has a more positive charge on the carbon in the carbonyl, while the dimethylamino group has the smallest positive charge, with the neutral methyl group in the middle. These results suggest that the substituent para to the reactive ester portion of the initiator potentially affect the electrophilicity by changing the local charge, as discovered through computation.
When examining the substituent effect of the ester portion of the initiator, there is a surprising result. With the case of the initiators that have the dimethylamide group on the benzoate, the substituent on the ester plays no role in changing the charge on the carbon of the carbonyl (Table 5.4). This result could be from the fact that the electron withdrawing group of the dimethylamide could account for the small change in charge that the ester substituent may cause through its strong electron withdrawing character. The difference in reactivity outlined earlier remains yet to be supported by the charge computation data and are believed to be caused by the stability of the leaving group, not the electrophilicity. Further studies on the transition states for the reaction between initiator and deprotonated monomer are in progress and will offer a better explanation of experimental results outlined above.

**Charges Reflecting Electrophilicity of Protonated and Deprotonated Monomer and Dimer**

Computation was also used to help understand the reactivity of the various species present when forming the active initiator species through the self-condensation mechanism. To do this, the charges of the carbonyl again were calculated for four different species that may exist throughout the polymerization that would lead to polymer growth (Figure 5.7).
Figure 5.7. Structures used to calculate charges on the atoms included in the ester group for the three monomers investigated.

Firstly, the charges of the two possible species regarding the monomer were calculated. As mentioned, the deprotonated and protonated versions of the monomer could exist in the solution and the results from these calculations can be seen in Table 5.5. Results from this table suggest that there is a difference between the charge on the carbonyl for protonated and deprotonated, with a more positive charge on the protonated monomer.

Table 5.5. Charges calculated for the protonated and deprotonated versions of the monomer with different ester groups.

<table>
<thead>
<tr>
<th>Atom (In Bold)</th>
<th>Monomer</th>
<th>Ester R Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methyl</td>
<td>Phenyl</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>-0.578</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>-0.595</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>0.841</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>0.815</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>-0.664</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>-0.716</td>
</tr>
</tbody>
</table>
This larger positive charge, like before could mean that the carbonyl is more positive, suggesting that this carbonyl is more electrophilic. The more electrophilic carbonyl, by conventional CGC theory means that that it is more reactive, which could be a source for the dimer as discussed earlier.

Next the charge is also calculated for atoms of the carbonyl for the two potential versions of the dimer formed by the coupling of two monomers. Below, in Table 5.6, the charges on the protonated and deprotonated versions of the dimer show that there is very little difference in charge on the carbon of the carbonyl. The high positive charge on the carbon atom of the carbonyl for both of the dimer structures than both protonated and deprotonated versions of the monomer structures suggest that a dimer could be more electrophilic and act as an initiator. It is believed that once the dimer forms, the polymerization is effectively initiated, due to the more reactive carbonyl at the end group and the results here support that claim.

Table 5.6. Charges calculated for the protonated and deprotonated versions of the dimer with different ester groups.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Atom (In Bold)</th>
<th>Ester R Group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Methyl</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>-0.575</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>-0.590</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>0.856</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>0.859</td>
</tr>
<tr>
<td>Protonated</td>
<td>O=C-OR</td>
<td>-0.621</td>
</tr>
<tr>
<td>Deprotonated</td>
<td>O=C-OR</td>
<td>-0.622</td>
</tr>
</tbody>
</table>

More computation studies are being performed to understand the transition state energies and activation energies associated with the reaction of monomer with potential initiators and findings will be reported in with these results in an upcoming paper submission.
5.4 Conclusions

Recent studies have demonstrated that reactivity of aminobenzoate monomers depend on the nature of the ester substituent greatly when employed in a chain growth condensation polymerization. More reactive monomers contain electron withdrawing substituents on the esters to produce more stable leaving groups and result in faster reaction kinetics. The increased reactivity of these esters posed interesting challenges, due to the possibility of the monomers to self-initiate and polymerize with no initiator. The challenge addressed herein was to understand the self-initiation behaviour and find initiators that allow for control to be achieved. Results from this study demonstrate that the relative amount of LiHMDS base can be used to slow, but not stop the self-initiation reaction with excess base slowing the self-initiation reaction the most. LDA, being a stronger base works for the polymerization, produced polymers with narrow distributions, but is not a good candidate, due to the high strength of the base. Literature has shown to previously utilized LDA to lithiate the ortho position of electron withdrawing groups on phenyl rings and this is undesirable, because it could cause side reactions and have the potential to lower conversions. Control over the polymerization was achieved by using the most reactive initiators, which have electron withdrawing substituents both on the initiator backbone and the leaving ester. Balancing the relative rates of initiation, propagation and self-condensation is key when attempting to use more reactive esters to produce CGC aramids.
6.1 Introduction

Surface coatings today have a wide variety of applications and rely on many technologies and methods to produce them. Typically, coatings are created by applying a premade solution of polymers or small molecules to a surface and allowing the film to dry, leaving a “physically” adsorbed polymer to the surface. Due to the relatively weak bond formed between the film and the surface, many of these systems experience thermal and solvolytic instabilities. As such, recently new processes have been developed to produce more impressive polymer films by chemically attaching polymer brushes to surface, and being able to grow polymers from the surface to enable the synthesis of films with more functionalities and structure.

The advent of polymer brushes, or polymers that are covalently attached to a surface at a high enough density to force the chains to adopt an extended conformation, has opened a new and exciting area of research. The research leading to the discovery of the most utilized controlled living radical polymerization (LRP) techniques, such as reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP), has demonstrated very impressive applications of polymer brushes including stimuli responsive behavior and the formation of complex architectures. Even though polymer brushes have been demonstrated to produce a wide variety of uses and applications, there remains a many different polymers and architectures that have not yet been realized, specifically brushes that contain polymers with more rigid backbone character, otherwise known as rigid rod polymers.

Coatings typically required to exhibit very impressive mechanical, thermal, and chemical properties are produced from polymers that are prepared separately and are then applied to a
surface in a post treatment. The polymers most frequently envisioned to exhibit these properties are poly(aromatic amides) or aramids. Conventionally, aramids are produced via a step-growth process, where aromatic diamines are reacted with aromatic diacid chlorides and performed in caustic solvents that are able to dissolve the produced polymer. While the step growth synthesis of aramids has proven to be very successful at producing solution based polymers, it is not suitable for the synthesis of polymer brushes. Previous polymer brush research has comprehensively detailed the need for use of a controlled chain growth polymerization technique to produce well-defined polymer brushes via the grafting from method. Attempts to produce polymer brushes using step growth polymerizations have led to non-uniform films with low grafting densities due to the fact that the surface modification proceeds by a grafting to type mechanism, rather than the necessary grafting from mechanism, and polymer formed by the step growth process usually have broad molecular weight distributions. Recently, there has been a significant amount of research investigating the development of new polymerization techniques to convert traditional step growth processes to more of a chain growth mechanism and this research has resulted in the discovery of the so called chain growth condensation (CGC) techniques.

The discovery of the CGC process was profound, in that it provides a way to produce polymers, typically prepared by step growth polymerization, with controlled molecular weights, narrow molecular weight distributions, enhanced functionality, and more complex architectures. In addition to these benefits, the CGC techniques are excellent candidates for surface-initiated polymerizations to prepare polymer brushes. As the CGC techniques allow for the preparation of well-defined polymers and occur via a living mechanism, they also satisfy the main requirements for producing polymer brushes. These techniques are also novel in that they allow for the synthesis of polymer brushes from polymers that have not been previously utilized, such as conjugated polymers and aramids.
Currently, there are two main CGC processes – activation/deactivation using substituent effects and catalyst transfer. Each of these processes is centered on the idea that a chain growth mechanism can be achieved if the monomer selectively reacts with the propagating chain end rather than reacting with other monomers. The theory behind the CGC techniques and the many new materials made using them has been extensively reviewed in the literature. Interestingly, despite the obvious potential of the CGC techniques for surface modification and in the preparation of polymer brushes, there are only a few reports in this area and all of them utilize the catalyst transfer process to produce conjugated polymers.

The challenge to produce polymer brushes using substituent effect CGC was first addressed in a previous paper by our group, where we demonstrated the preparation of the first ever aramid brushes.\textsuperscript{6} The aramid brushes were prepared by first developing a functional initiator for substituent effect CGC that has the ability to attach to silica surfaces. This initiator utilized the dual functionality of a para-carbonyl functionality, with one side used to attach to an amino-silane, for surface modification, and the other side functionalized with an activated ester group. The versatility of this newly designed initiator was demonstrated by its deposition on both flat and high surface area silica surfaces, followed by the preparation of well-defined poly(\textit{N}-octyl-p-benzamide) brushes using substituent effect CGC.\textsuperscript{126} However, while these results proved that brushes could be produced using this technique, the thicknesses produced were not very impressive and appeared to be self-limiting.

Based on observations during the polymerization, two main causes for the limited thickness of the poly(\textit{N}-octyl-p-benzamide) brushes were proposed. The first issue apparent was the formation of a hazy, white film on the silicon wafer during the polymerization. It was observed that this film could not be removed by washing with common organic solvents, including the solvent used for the polymerization, but was completely removed when a polar protic solvent (e.g. water or alcohols) was used. It was hypothesized that this film was produced by the insoluble lithium
methoxide by-products formed whenever a monomer attaches to the end group of the polymer brush. This insoluble film can then collect on the surface of the brush and block the end group from continuing to add monomer, which resulted in the limited thicknesses obtained. The second issue identified was the poor reactivity of the methyl ester monomer in general. Previous studies investigating solution-based polymerizations of the methyl ester monomer demonstrate that while it does indeed produce polymer, the rate of polymerization is much slower rate when compared to phenyl ester-based monomers. Both of these issues were investigated in this study, in an attempt to produce thicker brushes, and the preliminary results are presented below.

6.2 Experimental

6.2.1 Materials

Lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS, 1.0 M) in tetrahydrofuran (THF), dimethylamine solution (2 M, THF), triethylamine (>99.5%), thionyl chloride (SOCl₂, >99.5%), anhydrous dichloromethane (DCM) (stabilized with 50-150 ppm amylene, >99.8%), octanal (99%), sodium triacetoxyborohydride (97%), tetraethylorthosilicate (TEOS, 98%), and MgSO₄ were purchased from Sigma-Aldrich. DCM, acetic acid, NaHCO₃, aqueous H₂O₂ (30%), pentane, and ethyl acetate were purchased from Macron. N-methylaminopropyltrimethoxysilane was purchased from Gelest, 4-(methoxycarbonyl)benzoic acid from Matrix Scientific, ethanol (200 proof, absolute) from Pharmco-AAPER, aqueous ammonia (28-30%) from Mallinckrodt Baker, ammonium chloride (99.9%) from Baker Scientific, methyl 4-aminobenzoate (98%) from Alfa Aesar, H₂SO₄ (95.0-98.0%) from EMD Performance Materials, and aqueous hydrofluoric acid (HF) (49%) from Fisher Scientific. Unless otherwise mentioned, all chemicals were used as received without further purification. THF and toluene solvents were purchased from Macron and were purified and dispensed through a PURE SOLV MD-4 solvent purification system (activated alumina, copper catalysts, and molecular sieves). Silicon wafers (prime grade, single side polished) were obtained from Wafer World, with only a native oxide.
6.2.2 Characterization

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained on a JEOL-500 S MHz spectrometer. Bulk infrared spectra were recorded on a Thermo Scientific Nicolet iS50 Fourier transform infrared (FTIR) spectrometer using a diamond attenuated total reflectance (ATR) crystal for bulk samples, while thin films on silicon wafers were measured using a Harrick Scientific VariGATR accessory (grazing-angle ATR (GATR)). Ellipsometric measurements were carried out on a VB-250 VASE series ellipsometer, with a HS-190 monochromator and a 70 degree angle of incidence. Refractive indices were fixed at 1.45 for all respective surface modifications and brushes and a thin film of silica on silicon model was used to calculate thicknesses. Contact angle measurements were recorded using a ramé-hart Standard Goniometer 200-00 using 10 µL drops of deionized ultra-filtered (DIUF) water. Images were processed using DROPImage software. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 using air at a flowrate of 30 mL/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Physical Electron 5800 ultra-high vacuum XPS-Auger spectrometer at Colorado State University. The incidence angle of X-ray was 45° with respect to the surface normal. Number average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$, PDI) were measured using a Viscotek GPCmax gel-permeation chromatography (GPC) unit (eluent: stabilized tetrahydrofuran (OmniSolv) with a flow rate of 1.0 mL/min using PLgel 5µm MIXED-C and MIXED-D columns: molecular weight range 200-2,000,000 and 200-400,000g/mol (polystyrene equivalent), respectively). A calculated dn/dc value of 0.156 was determined and used during the analysis. Stöber particles were characterized and sizes were measured using a JEOL JSM-7000F scanning electron microscope (SEM) with a Schottky cathode field emitter at 20kV. Samples were sputtered with gold to make conductive.
6.2.3 Synthesis of Methods

6.2.3.1 Synthesis of Monomer and Initiator

Phenyl 4-(octylamino)benzoate (P-OAB)

Synthesized from literature. Phenyl 4-aminobenzoate (6.0 g, 28.3 mmol), octanal (3.62 g, 28.3 mmol), acetic acid (2.4 mL, 42.4 mmol), and sodium triacetoxyborohydride (7.8 g, 36.8 mmol) were used. Product: as white crystals; mp 112-113 °C, (7.3 g, yield 79%).

$^1$H NMR (500 MHz, CDCl$_3$, δ): 8.0 (d, J = 8.9 Hz, 2H, ArH), 7.4 (t, J = 8.1 Hz, 2H, ArH), 7.25 (t, J = 8.1 Hz, 1H, ArH), 7.18 (d, J = 8.1 Hz, 2H, ArH), 6.59 (d, J = 8.9 Hz, 2H, ArH), 4.2 (br, 1H), 3.2 (t, J = 7.4 Hz, 2H), 1.6 (q, J = 7.4 Hz, 2H), 1.42-1.22 (m, 10H), 0.88 (t, J = 7.4 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 167.3, 152.1, 131.4, 117.6, 111.1, 51.3, 43.2, 31.7, 29.2, 29.16, 29.1, 27.0, 22.5, 14.0.; FTIR (ATR): ν = 3380 (Ar-NH-R), 2921, 2852 (C-H), 1691 (O-C=O), 1594, 1275, 1163, 1075, 742 cm$^{-1}$.

Phenyl 4-((3-(dimethoxy(methyl)silyl)propyl)(methyl)carbamoyl)benzoate (MDMS-Amide-P)

A similar procedure to that reported in literature$^{196}$ was used with N-methyl-3-(trimethoxysilyl)propan-1-amine used in place of the 3-(triethoxysilyl)propan-1-amine. Briefly, a solution of N-methyl-3-(trimethoxysilyl)propan-1-amine (1.0 g, 5.18 mmol) and triethylamine (0.73 g, 7.25 mmol) in anhydrous DCM (20 mL) was added to a solution of the acid chloride (methyl 4-(chlorocarbonyl)benzoate) (1.1 g, 5.55 mmol) in anhydrous DCM (20 mL). The solution was refluxed for 1.5 h followed by concentration in vacuo. The crude reaction mixture was purified by flash column chromatography on silica gel (pentane/ethyl acetate 1:1) Product: as a white solid, mp. 65-66 °C, (1.2 g, yield: 66%).

$^1$H NMR (500 MHz, CDCl$_3$, 25°C): δ = 8.05 (d, J = 8.19 Hz, 2H), 7.42 (d, J = 8.05 Hz, 2H), 3.91 (s, 1H), 3.57, 3.49 (2s, 9H), 3.51, 3.15 (2t, J = 7.36 Hz, 2H), 3.05, 2.88 (2s, 3H), 1.77, 1.61 (2m, J = 7.05, 2H), 0.68, 0.37 (2t, J = 8.02, 2H);

$^{13}$C NMR (125 MHz, CDCl$_3$) 170.6, 170.0, 166.0, 141.0, 130.6, 130.5, 129.5, 129.4, 126.7, 126.5, 53.2, 52.0, 50.2, 49.6, 37.0, 32.3, 21.2, 19.9, 6.18, 5.65 ppm; FTIR (ATR): 2942.4, 2840.1, 1721.2, 1632.7, 1434.7, 1401.4, 1274.1, 1189.5, 1069.6, 813.3, 785.1, 733.5 cm$^{-1}$.
6.2.3.2 Polymerization Methods

Deposition of MDMS-Amide-P Initiator on Silicon Wafers Surface

Fresh cut silicon wafers were cleaned with freshly made piranha solution (30:70 30% H₂O₂:conc. H₂SO₄) at 100 °C for 2 h. Caution: piranha solution is extremely caustic and should be handled with care. The wafers were removed and washed 3 times with DIUF water and dried under filtered air. The wafers were then placed directly into 10 mL reaction flasks. Anhydrous toluene (10 mL) and MDMS-Amide (85 mg, 0.2 mmol) were placed in the flask and it was capped with a glass stopper. The solution was heated to 100 °C for 2 h. The wafers were then removed, washed twice with fresh toluene and dried under filtered air. The wafers were then annealed in a 120°C oven (air) for 30 min to remove any condensation products.

Preparation of 500 nm Stöber Silica for High Surface Area Samples

Stöber particles, approximately 500 nm in diameter, were synthesized by adding 300 mL of absolute ethanol and aqueous ammonia (100 mL, 1.45 mol) into a 500 mL round bottom flask with a stir bar. TEOS (25 mL, 112 mmol) was added at room temperature while stirring vigorously. After 12 h, the particles were washed four times with anhydrous ethanol using sonication/centrifugation wash cycles. The particles were then dried in a vacuum oven, calcined in tube furnace at 600 °C for 12 h, re-dispersed in DIUF water and freeze dried to a fine white powder. Particles were characterized using SEM.

Deposition of MDMS-Amide-P Initiator on Stöber Silica Surface

3 g of calcined Stöber Silica was placed directly into a 500 mL round bottom reaction flask. Anhydrous toluene (350 mL) and MDMS-Amide (0.8 g, 4.71 mmol) was added to the flask, which was then capped with a glass stopper. The solution was heated to 100 °C for 2 h with stirring. The particles were then washed with repeated centrifugation/suspension twice in toluene and once in THF using glass centrifuge tubes. The resulting powder was dried in a vacuum oven to give an off-white powder. Particles were characterized using SEM.
Formation of Polymer Brushes on Silicon Wafer Surface

MDMS-Amide-P modified wafers were placed into a 10 mL reaction vessel along with a stir bar and monomer (P-OAB) (0.16 g, 0.5 mmol) and the vessel then capped with a septum. The flask was purged with argon for 10 min and filled with degassed, anhydrous THF (10 mL). The reaction was placed in an ice bath and allowed to cool for 10 min at 0 °C. LiHDMS (1.1 mmol, 1.1 mL) was then added to deprotonate the monomer and start the polymerization from the surface. The reaction was allowed to proceed for a desired time (6 h) and the wafers were then removed, washed with DCM, THF, and DIUF water and dried under filtered air. The wafers were finally annealed in an oven (120°C) for 30 min before characterization.

Formation of Polymer Brushes on Stöber Silica Surface

MDMS-Amide-P modified Stöber silica (1 g) was placed into a 100 mL Schlenk flask reaction vessel along with a stir bar and monomer (P-OAB) (0.26 g, 1 mmol) and the vessel then capped with a septum. The flask was purged with argon for 10 min and then degassed, anhydrous THF (10 mL) was added. The reaction was placed in an ice bath and allowed to cool for 10 min at 0 °C. LiHDMS (1.0 mmol, 1.0 mL) was added to deprotonate the monomer and start the surface polymerization on the silica. The reaction was allowed to proceed for a desired time 6 h and quenched with saturated ammonium chloride solution. The polymer-coated Stöber silica was isolated by repeated centrifugations and washings with DIUF, DCM, and THF using glass centrifuge tubes and sonication. The organo-silica particles were then dried in vacuum oven (120 °C) for 1 h before characterization.

6.3 Results and Discussion

6.3.1 Evidence of Insoluble Lithium Hydroxide Film in Methyl Ester Monomer System

To gather more information on the chemical makeup of the insoluble film observed in the preliminary brush study published in literature by our group (Chapter 3 in this document), XPS was performed on the polymer modified wafer after rinsing with THF to remove physisorbed solution reagents and after washing with water (Figure 6.1 and Table 6.1). The wide-scan data
collected shows all of the expected elements for the polymer brush: carbon, nitrogen, and oxygen for the sample washed with either THF or water (Table 6.1).

![Figure 6.1. Wide-scan X-ray photoelectron spectra of the neat polymer brush film as obtained from polymerization solution after rinsing with THF (left) and spectra of the film after rinsing with water (right).](image)

Table 6.1. Collected XPS wide scan values of atomic percentages of the neat polymer brush film after being removed from solution and rinsed with THF along with the values obtained after washing the insoluble film away with water.\(^5\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Neat Brush</th>
<th>H$_2$O Wash</th>
<th>H$_2$O Wash</th>
<th>H$_2$O Wash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Collected</td>
<td>Adjusted</td>
<td>Theoretical</td>
<td></td>
</tr>
<tr>
<td>C 1s</td>
<td>47.7</td>
<td>84.6</td>
<td>88.9</td>
<td>88.2</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>34.7</td>
<td>8</td>
<td>5.7</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Li 1s</td>
<td>15.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>N 1s</td>
<td>1.6</td>
<td>5</td>
<td>5.4</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Si 2P</td>
<td>0.5</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Atomic percentages were adjusted by removing the expected percentages of oxygen that would exist from the native oxide. The ratio of SiO$_2$ Si/Metal Si was 32%.
However, for the sample washed with THF only, lithium was also detected and was present at a relatively high amount, 15.8%. Whereas, the XPS results for the sample after washing with water shows that no lithium is present and that the adjusted atomic percentages measure closely match the theoretical percentages for the polymer. These results confirm our initial hypothesis that a film of organic-insoluble lithium salt is depositing on the wafer over the course of the polymerization and that this film may be responsible for the limited thickness in the initial polymer brushes.

6.3.2 Synthesis of Silane Based CGC Initiator (MDMS-Amide-P)

The results from our solution-based study on the effect of monomer structure on substituent based CGC (Chapter 4) demonstrated that structure of the ester group on the monomer has a dramatic effect on the solubility of the reaction by-products and on the polymerization kinetics. Specifically, it was observed that, when compared to the methyl ester monomer, monomers with phenyl ester derivatives all produced soluble by-products over the course of the polymerization and the reaction rates were also much higher. As such, it was concluded that the phenyl ester derivative monomers would be good candidates to use when attempting to overcome the issues encountered during the initial polymer brush study.

Firstly, a new silane CGC initiator was designed to incorporate two improved functionalities. The first improvement incorporates the dimethoxy functionality on silane attachment portion of the initiator to produce a more uniform deposition. The two hydrolyzable groups in place of the three used in the original initiator, allows for less branching and crosslinking of the silane in solution, which leads to a more uniform film on the surface. The second functionality that was improved was with the replacement of the methyl ester group with a phenyl ester moiety. This improved functionality allows for a more reactive initiator on the surface and the lithium phenoxide produced as a by-product of the initiation process demonstrates excellent solubility in the reaction media. The synthesis of MDMS-Amide-P is portrayed in Scheme 6.1.
6.3.3 Deposition of MDMS-Amide-P on to SiO$_2$/Si Wafers

The newly prepared initiator for surface-based CGC was deposited on piranha-cleaned silicon wafers in hot anhydrous toluene, rinsed with fresh toluene, dried, and annealed to remove the condensation products and secure the initiator layer to the wafer (Scheme 6.2). The deposited initiator was characterized using goniometry, ellipsometry, and FTIR spectroscopy. Goniometry results from the wafers before and after surface modification showed an increase from a surface that is essentially completely wetted (~1-3°) for clean wafers to a contact angle of 53±3° for the wafers with the deposited MDMS-Amide-P initiator. These results are consistent with a change from the initial hydroxylated silicon surface to the more hydrophobic phenyl ester. Ellipsometry measurements show that the thickness of the film increases from the initial silica layer thickness of 1.5±0.1 nm to a thickness 2.9±0.1 nm, using the same SiO$_2$ model to fit the data, after deposition of the initiator. The 1.4 nm MDMS-Amide-P film is very close to the 1.5 nm calculated film thickness of a monolayer of MDMS-Amide-P molecules that are perpendicular to the surface, also suggesting very little crosslinking and aggregation of the silane molecules on the surface. The small error in the measurements also demonstrates a good model fit to the ellipsometry data, also suggesting a uniform MDMS-Amide-P film.

Scheme 6.2. Deposition of MDMS-Amide-P initiator on silicon wafer.
GATR-FTIR performed on the deposited TMS-Amide-P film on silicon wafers showed very small peaks, indicating that the initiator is present, but in a much smaller concentration than the previous methyl ester study. These results are suggest that the smaller amount of initiator on the surface could be attributed to the more defined layer formed by the dimethoxy silane initiator, instead of potential crosslinking/aggregating and higher density of species that was potentially present in the preliminary study with the trimethoxy silane (Chapter 3). The over-layed spectra for the neat MDMS-Amide-P and the initiator thin film on silicon can be viewed in Figure 6.2.

![Figure 6.2. ATR-FTIR spectra of neat MDMS-Amide-P overlaid with a spectra of the deposited MDMS-Amide-P thin film obtained using GATR-FTIR spectroscopy.](image)

Pertinent absorption bands indicative of the MDMS-Amide-P molecule are evident with peaks at approximately 2850 and 2930 cm$^{-1}$, which correspond to the CH$_2$ stretching and C-H vibrations, respectively, along with peaks at 1730 cm$^{-1}$, pertaining to the ester stretch, and 1650 cm$^{-1}$, corresponding to the amide carbonyl stretch. The peaks not matching the neat MDMS-Amide-P spectrum at 1200 cm$^{-1}$ and 900-800 cm$^{-1}$ are present in a spectrum for clean, unmodified silicon
wafers and can be assigned to the Si-O-Si stretch and Si-O-H stretch & bend modes for silica, respectively. The peak at 1100 cm\(^{-1}\) is a peak that shows up after the silane deposition and can be assigned to chemisborbed Si-O-Si from the MDMS-Amide-P.

### 6.3.4 Growth of Aramid Brushes using CGC from Surface-Immobilized Initiators on Flat Silicon Substrates Employing the Phenyl Ester Monomer

To determine the effectiveness of the surface-immobilized MDMS-Amide-P initiator for CGC, aramid brushes were grown by immersing the initiator-modified silica wafers in a solution of deprotonated monomer in THF at 0 ºC (Scheme 6.3). After the polymerization, the modified wafers were extensively cleaned via sequential solvent treatment to remove excess monomer and ensure characterization was focused on the surface-immobilized polymer. The formation of surface initiated polymer chains was confirmed using goniometry, ellipsometry, and FTIR spectroscopy. Goniometry measurements demonstrated that the contact angle of the wafer increased from 53 ± 3º to 78 ± 3º after polymerization, suggesting a more hydrophobic surface indicative of the octyl solubilizing groups that is incorporated on the surface as part of the repeating unit of the polymer chain. The contact angle measurements for the brush film is comparable to results for a spin-coated film of poly(2), 80 ± 2º. GATR-FTIR measurements (Figure 6.3) also indicate that the surface-immobilized polymers had near perfect spectral overlap to that of polymer prepared in solution using the CGC. The pertinent peaks are the C-H stretches and bends near 2850 and 2930 cm\(^{-1}\), along with the small signal at 1730 cm\(^{-1}\) indicative of the ester end group, and the large amide stretch at 1650 cm\(^{-1}\), corresponding to the more common amide linkages found along the polymer backbone. The free polymer used for this spectrum was produced using the DMA-P initiator at a feed ratio of 50:1 P-OAB:DMA-P, as produced for previous studies (Chapter 5). The ester stretch present in the free polymer indicates that the ester end group is present for a relatively low degree of polymerization, suggesting that the polymer brush is at a much larger molecular weight than DP = 50, due to the lack or very small presence of the ester stretch in the brush sample.
Scheme 6.3. Growth of aramid brushes from MDMS-Amide-P bound initiator from silicon wafers.

Figure 6.3. Comparison between the FTIR spectra of polymer grown in solution and the thin film aramid brush on silicon wafers.

The thicknesses of the samples were measured using ellipsometry. Initial measurements using silica as the model material, demonstrated that there was a poor fit of the data to the model. After further investigation, the data was fit with a more appropriate Cauchy model, where the
thickness and index of refraction could be determined. When using the Cauchy model, it was determined that aramid brushes created using the technique above employing the phenyl ester initiator (MDMS-Amide-P) and the phenyl monomer (P-OAB) were measured to be approaching 5 times thicker than films achieved using the methyl ester method (Chapter 4). The Cauchy model allowed for a more appropriate fit of the data to the model with an extracted index of refraction for aramid brush films being 1.54, instead of using silica’s index of refraction equaling 1.45. With this new model, thicknesses were measured to be over 50 nm, with brush thicknesses varying up to 5 nm depending on the polymerization sample under the same conditions. Thicknesses as a function of time are to be examined with future work as these results presented here are only preliminary.

6.3.5 Growth of Thicker Aramid Brushes using CGC from Surface-Immobilized Initiators on High Surface Area Silica

In order to gain more information on the surface-initiated aramid brushes, brushes were also grown from silica nanoparticles that had been modified with the MDMS-Amide-P initiator (Scheme 6.4). Relatively large diameter Stöber silica nanoparticles (~500 nm) were synthesized, calcined, rehydrated, and freeze dried to mimic the properties of flat silicon wafers. The surface initiator was deposited on the Stöber silica by stirring the particles in hot anhydrous toluene with the MDMS-Amide-P initiator. Brushes were grown from the cleaned and dried initiator-modified particles by placing them in a flask with the monomer, THF and base at 0 °C to start the reaction from the surface (Scheme 6.4). After extensive washings and centrifugations, the particles were dried and characterized using TEM and TGA.
Scheme 6.4. Deposition of MDMS-Amide-P initiator on silica nanospheres along with polymer growth from surface modified Stöber silica nanoparticles using CGC polymerization. Surface diagrams and curvature not to scale.

In addition, the calcined silica particles, particles modified with the MDMS-Amide-P initiator, and the particles after a representative surface-initiated CGC polymerization were all analyzed using TGA (Figure 6.4). The TGA trace for particles coated with MDMS-Amide-P initiator lost approximately 0.5 wt.% of mass, when compared to the calcined silica which corresponds to approximately 2 initiator molecules/nm$^2$ on the surface of the silica particles. This calculation was performed by converting the wt.% lost in TGA to a mass using the original mass of particles, converting this mass to a number of molecules using the burnable portion molar mass of the surface-immobilized initiator (297 g/mol) and dividing the number by the surface area of the 500 nm spherical particles (4.53x10$^{18}$ nm$^2$/g). When compared to the TGA results obtained from the methyl ester system, the initiator density for the MDMS-Amide-P system is roughly half of what was observed for the TMS-Amide results in Chapter 3. This can be explained by the lower amount of grafting points for MDMS, with only two reactive groups that can couple with the surface and less degree of crosslinking possible.
The decomposition profile of the grafted aramid brushes became more pronounced with the onset of degradation at 480°C and exhibited a sharper decomposition that is more stable than the TGA profile of free polymer and methyl ester brushes, which decomposed at 400°C (Figure 6.5). The major difference between the onset of decomposition could be attributed to ordering of the aramid chain, that could potentially allow for a more stable material. The improved initiator layer, using the difunctional silane could be contributing to a more uniform initiator layer, where subsequent brushes could pack in a more ordered arrangement. Another possibility is that the molecular weight of the grafted polymers could be much larger than the methyl ester brushes or the free polymer, so a higher molecular weight could contribute to a higher decomposition temperature, and future studies will examine if this could be the case using a degrafting scheme.

The thickness of the polymer film on the silica particles was determined using TEM and the results indicated that the polymer modified particles had a core shell structure (Figure 6.5). From
the TEM images, the aramid brush thickness was measured to be 10±1 nm and appeared to be very uniform across the surface of the particle. The lower thickness of the aramid brush on the silica nanoparticles, compared to the silicon wafers, is attributed to the much higher concentration of initiators on the silica particles relative to the amount of monomer present in the reaction mixture. The silicon wafers have roughly 6 orders of magnitude less initiator molecules present in the reaction, so these initiators would see more monomer over the course of the reaction when compared to the nanoparticles.

![TGA traces of particles after a representative CGC polymerization, along with free polymer. Inset is a TEM micrograph of a core-shell brush structure on a spherical silica nanoparticle.](image)

Figure 6.5. TGA traces of particles after a representative CGC polymerization, along with free polymer. Inset is a TEM micrograph of a core-shell brush structure on a spherical silica nanoparticle.
As the polymer molecular weight, which is proportional the thickness for polymer brushes, is a function of the ratio of monomer concentration to initiator concentration, the polymer on the flat wafers should have a higher molecular weight and, hence, brush thickness, which is indeed the case. As mentioned previously, the thickness of the shell layer seems to be very uniform on the particles, suggesting a well controlled polymerization process and a visible thickness is evident for the phenyl brushes. When compared to the results for the methyl ester system no obvious shell is observed, (Chapter 3) the aramid brushes produced from the phenyl ester monomer proved to be much thicker on both the silicon wafer and high surface area particles. Even though there was no obvious core-shell structure for the methyl ester system, polymer was still isolated from the particles using the degrafting approach and measurable material was removed in the TGA, reaffirming that polymer was grafted to the particles, but in much smaller quantities.  

6.4 Conclusions

Improvements upon a preliminary study were employed to produce thick poly((N-octyl)benzamide) brush films via the surface-initiated chain growth condensation process. The original brush study employed a methyl ester group that successfully was used to create the first examples of aramid brushes in literature using the CGC technique, but issues with reactivity and solubility limited the progress in forming thick brushes. After investigation into the polymerization mechanism and process further, improvements to the initiator and monomer by replacing the methyl ester with a more reactive phenyl ester were discovered to produce the same polymer, with thicker results and more soluble byproducts. The replacement of the monomer with a more reactive phenyl ester, along with employing an initiator that has a dimethoxysilane functionality, in place of the trimethoxy version, so a more reactive and more uniform initiator layer could be produced for the reaction. Film thicknesses approaching 50 nm on silicon wafers and 10 nm on Stöber silica were achieved using the improved method. This study is not fully completed, as it is comprised of only preliminary data. Further experiments are being conducted to further characterize this system, by examining the kinetics of the system on both high surface area
particles and silicon wafers. Degrafting strategy using hydrofluoric acid will also be used to study the molecular weight and molecular weight distributions, as what was conducted in the Chapter 3 to allow for a determination of the grafting density of the chains.
CHAPTER 7
CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

Polymer brushes have demonstrated to be excellent improvements upon conventional coating
technologies. Covalently attaching polymers have evolved from a grafting to approach to a more
novel grafting from technique, where polymers are grown in a controlled, chain growth manner
from a surface bound initiator. Improved polymer coatings have been demonstrated to be more
solvolytically stable and allow for functionalization of many surfaces and serve many purposes.
Polymer brushes have been demonstrated originally when controlled, living free radical (LRP)
polymerizations were adapted to be grown off of a surface by utilizing a surface-bound initiator.
The most common techniques utilized are atom transfer radical polymerization (ATRP) and
reversible addition-fragmentation chain transfer (RAFT) polymerization. The reason for this
radical polymerization dominance has its origin with the concept that surface initiated controlled
polymerizations rely on a chain-growth process. There remains a wide variety of polymer brushes
that have not been realized to date, due to the fact that there are many ways to produce polymers.

The two most common ways to produce polymers is either with a step growth process, where
monomers condense in a random sequence with no control over molecular weight or molecular
weight distribution. The other procedure used to produce polymers with a chain growth process,
where an initiator is employed to start the polymerization and monomers add at a propagating
end group of the polymer. Radical polymerizations rely on activation and deactivation of the active
end group to control the propagating radical, while chain growth condensation polymers rely on
converting step growth to chain growth process by ensuring the polymer end group is more
reactive than the reactive group on the monomer.
The chain growth condensation process is a relatively new concept to the scientific community and especially the polymer community. One of the most exciting opportunity that CGC provides is the ability to produce never before envisioned polymers in a chain-growth manner. This process, by virtue produces polymers conventionally synthesized using the step growth condensation process in a chain growth manner, which allows for the potential to produce controlled surface-initiated polymer brushes. This exciting work pioneered by Yokozawa and coworkers has laid the groundwork for the basis of this thesis.

The opportunity to grow never before realized polymer brushes has allowed the research herein to be conducted. The work presented in these chapters is the first examples of CGC being applied to surfaces to create novel, surface-initiated aramid brushes. This process was pioneered by developing new initiators that have the ability to attach to silica surfaces. The effectiveness of the new initiators was studied using a solution analog, and proved to be successful when compared to literature. Poly(N-octylbenzamide) brushes were successfully grafted from silicon wafers and high-surface area silica nanoparticles and progress was monitored using FTIR, ellipsometry, TGA and GPC.

Preliminary aramid brush work demonstrated that CGC aramid brushes are indeed possible, but results did not meet the expectation of very thick films. The work supporting the preliminary results employing the methyl ester monomer demonstrated that the polymer brushes would grow to self-limiting thicknesses, with growth occurring in a controlled manner, but would slow and eventually stop at a critical thickness. Investigation into the cause of this undesirable result yielded a formation of an insoluble film that forms on top of the freshly made brush. Further investigation returned that the water-soluble film contains lithium using XPS. The blocking film was determined to be an insoluble lithium methoxide, indicating that the methyl ester monomer was not the best candidate for brush work.
The original hypothesis when envisioning these polymer brushes was that since there is no polymer termination mechanism, with chains potentially elongated with the end groups near the brush/solution interface, the brushes should theoretically grow without interruption to yield very thick polymer films. More work was completed to improve both the solubility of the condensation products and improve the kinetics of the system, so the original hypothesis can be achieved.

Further work presented in the thesis encompassed a study investigating the effect of the ester substituent on the polymerization performance. Various ester groups consisting of n-alkane groups, branched alkanes, and substituted phenyl esters were examined by polymerizing the monomers of interest and obtaining kinetic and qualitative solubility data. Pertinent results from this study, along with computational results demonstrated that the reactivity of the monomer end groups rely more on the stability of the leaving group than the electrophilicity of the attacked ester carbonyl. This theory supports the claim that understanding of the chain-growth condensation method theory is multifaceted when examining the reactivity of particular reacting species. Results from this study demonstrate that the electron withdrawing groups such as the trifluoromethyl phenoxide stabilizes the negative charge much more than electron donating groups such as the methoxy group for example. The reactivity of the monomers scales much more closely to the inverse of the pKa of the conjugate acid. The lower the pKa of the acid, the more stable the conjugate base, and therefore the more stable the leaving group when considering them in a nucleophilic acyl substitution reaction that is studied in this polymerization. This study also reports that phenyl derivatives produce more soluble condensation products, post polymerization, suggesting that the phenyl derivatives are better choices for potential brush systems.

As mentioned, more reactive monomers such as trifluoromethyl phenyl and phenyl ester containing monomers tend to polymerize much faster and create more soluble Lithium phenoxides, and are potential candidates for surface-initiated polymerizations. However, it was noticed that these monomers were observed to be so reactive that they have the tendency to self-condense
and polymerize without the presence of an initiator. This was realized to be an issue, due to the
notion that brush polymerizations require a monomer solution to be unreacted and deprotonated
and remain in that state throughout the course of the polymerization from the surface. A further
study investigated the control over polymerizations of more reactive monomers. Experiments that
investigated the self-condensation rates were completed and demonstrated that the more reactive
trifluoromethylphenyl monomer self-condensed much faster than the phenyl ester and at much
colder temperatures. Certain tactics such as using excess base and stronger bases was also
attempted to slow this process of self-condensation. When using one equivalent of the more
conventional LiHMDS base to deprotonate the monomer the polymer would self-condense and
polymerize at an appreciable rate, but slower than a reaction with an initiator. When excess base
was employed by using 10 times excess LiHMDS, the self-condensation would occur at a much
slower rate, suggesting that the excess base could deprotonate more of the monomer, thus
creating more deactivated monomer species.

When using a much stronger base, LDA, with an initiator, polymer was also produced, but the
reaction would not reach completion. These results were interesting, due to the contradiction that
was observed in literature, where LDA was claimed to be “too nucleophilic” for the reaction and
would replace the end group of the polymer with an inert amide moiety. The effect of initiator was
also investigated to examine which initiator substituent factors best influence the control over the
polymerization of more reactive monomers. Results from this study showed that polymers
produced from the most reactive initiators were the most controlled with the most narrow
molecular weight distributions and controllable molecular weights. The most reactive initiators
contained ester groups with the most stable electron withdrawing leaving groups and electron
withdrawing groups on the initiator. The results collected from the previous studies has allowed
for the design and implementation of an improved polymer brush system.
Finally, the novel brushes demonstrated earlier in the thesis were improved upon by implementing the lessons learned while broadening the understanding of the chain growth condensation technique. More reactive monomers were employed, while changing the initiator moiety that yields fast initiation relative to propagation to produce much thicker brushes in a shorter amount of time. The results demonstrated as a product of this research has laid the foundation for the development of more functional and improved aramid brush films and some potential work envisioned as an extension of this thesis is presented in the next section.

7.2 Future Work

The development of novel aramid brushes from theory to practice outlined in this thesis has demonstrated that polymer brushes can be assembled from new processes, and are solely possible by employing the chain-growth polymerization technique. Future work utilizing this process does not necessarily limit the research to strictly aramids. This work demonstrates that brushes theoretically can be assembled from any polymer that utilizes the chain growth method; this includes the wide variety of not yet realized chain growth condensation polymers that are reported in literature (Chapter 2).\textsuperscript{4, 112, 113} There is a vast amount of research that can be performed to produce polymers with an incredible variation in structure and properties. When examining the review articles on CGC brushes, the long list of polymers produced using the CGC via substituent method would be a great start when choosing a potential brush architecture for a desired application. Brushes would then be realized when the more activated initiator is applied to a surface and allow the polymerization to ensue.

One of the most pertinent studies that could be performed on the same polymer system studied throughout this thesis would be to study the structure of the surface brushes. It would be important to understand the structure of the polymer brushes in more detail to see if the rigid polymer backbones are, indeed aligned with one another to give a fully extended chain. This structure can be probed using neutron scattering measurements and small angle x-ray scattering
(SAXS). Other experiments can be conducted to see if the end group of the chains are actually
located near the surface and this can be done using XPS to see if the ester oxygen carbonyls are
located near the surface of the film using multi angle measurements.

When the research on aramid brushes is considered, future work has a wide variety of paths
to take. One of the most interesting routes to take would be to create polymer brushes that mimic
the very impressive properties of the well-known Kevlar® or Nomex® materials. The impressive
properties stem from the secondary amide structure of the repeat unit, where the amide linkage
contains a hydrogen side group that is available to hydrogen bond to adjacent rigid polymer
backbones. This robust structure offers the impressive thermal and chemical stability that is
observed with these materials. The potential to create a brush with these characteristics would
be interesting not just to materials scientists, but also brush simulation scientists, due to the liquid
crystal behavior of the ordered chains. This polymer has been produced in solution by
polymerizing a “protected” sidechain that is then cleaved with strong acid and these polymers
could be produced off of a surface to yield this Kevlar-like polymer brush. Future work would be
to understand the true structure of these brush films, since there is a potential to create more
aligned and ordered films, due to the rigid nature of the polymer backbone.

Other interesting future work could encompass changing the solubilizing group to contain
varying functionality, such as a more hydrophilic glycol sidechain, or hydrophobic perfluoro group.
These brushes would allow for a change in the surface properties of the more robust version of
brush and tailor the film for varying applications. The combination of substituting the aramid
backbone with protecting groups and functional groups was outlined for the production of
polybenzoxazole and would be a very interesting brush system to investigate, due to the high
degree of rigidity and ordering that may arise from these structures.

Future work could also include the formation of block copolymer rigid rod brushes or a
combination of rigid rod/random coil brushes using the controlled techniques mentioned in the
background. The synthesis of these very advanced structures could lead to applications never before imagined by using combined properties of rigid and flexible chains fixed to a surface to allow for more complex architectures such as responsive gates and channels for example.

Future work is envisioned to utilize these brushes in hybrid material applications, or composites. The impressive strength of similar materials emanates from the rigid and strong backbone nature. For example, if these brushes truly are elongated and, composite materials can be produced by end-group coupling to produce a network solid that has improved mechanical properties, due to the covalently bonded, elongated chains in line of the force applied (Figure 7.1).

Scheme 7.1. Potential method to crosslink aramid-modified silica particles through the ester end group functionality.

Use of aramid brushes in membranes, specifically reverse osmosis membranes are key to their function. The tailorability of the side chains of the polymer also would be an improvement upon the issues surrounding the chemical stability of secondary aromatic amides under chlorinated and other harsh conditions that are present in contaminated water. Specifically, the use of tertiary amides is important to limit the potential for N-chlorination reactions to occur via Orton Rearrangement. The tertiary and functionalized amides would allow for more stable, and thus, more robust coatings. Aramid brushes would allow for in-situ formation of aramid thin films that are covalently attached and functionalizable. Allow for growth off of a ceramic support
material, as opposed to cellulosic or polymeric substrates, which are susceptible to compaction and deformation from the high pressures required to purify the water at the atomic level (Figure 7.1).

Figure 7.1. In-situ grafting from technique allows for growth of polymer films on the inside of pores, which would be possible to make aramid-coated porous ceramic composites for separation technologies.
REFERENCES


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Figure A.1. ATR-FTIR spectra of unmodified, TMS-Modified, and polyaramid brushes on Stöber silica.
Figure A.2. TGA traces of free polymer and brush on Stöber silica.
Monomer and Initiator Precursor Synthesis

Aminobenzoate monomers with varying ester groups were synthesized using the following general procedure.

*Preparation of alkyl esters*

\[
\text{Methyl 4-aminobenzoate, (B1a) - commercially available}
\]

Representative procedure synthesis of alkyl aminobenzoate precursors (Fisher Esterification): (B1b-B1d)

Ethyl 4-aminobenzoate, (B1b)

A representative procedure is to dissolve 4-aminobenzoic (5g, 36.5mmol) into the corresponding alcohol (Ethanol, 200 mL, 3.4 mol). Concentrated sulfuric acid was then added (12 mL, 225 mmol) slowly. The mixture was refluxed until the white solution turned clear and colorless, indicating that the ester was formed. A portion of the alcohol was removed under vacuum, and
the resulting mixture was slowly poured into aqueous bicarbonate slowly. The resulting precipitate was filtered, rinsed with DI water, and dried. The isolated product required no further purification. Product: as white crystals; mp 89-90 °C, (4.5 g, yield 75%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.84 (d, $J = 8.7$ Hz, 2H; Ar H), 6.64 (d, $J = 8.7$ Hz, 2H; Ar H), 4.3 (q, $J = 7.2$ Hz, 2H), 4.1 (b, 2H, NH$_2$), 1.35 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 166.8. 150.7, 131.7, 120.2, 113.8, 60.4, 14.52; FTIR: ν = 3419, 3336, 3219, 2983, 2899, 1678, 1593, 1272, 1170, 1024, 845, 770 cm$^{-1}$.

Propyl 4-aminobenzoate (B1c)

Aminobenzoic acid (5 g, 36mmol), n-propanol (200 mL, 2.6 mol), concentrated sulfuric acid (12 mL, 225 mmol) were used. Product: as white crystals; mp 74-75 °C, (4.3 g, yield 65%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.84 (d, $J = 8.7$ Hz, 2H; Ar H), 6.64 (d, $J = 8.7$ Hz, 2H; Ar H), 4.21 (q, $J = 7$ Hz, 2H; CH$_2$), 4.2 (b,s, 2H, NH$_2$), 1.75 (m, $J = 7$ Hz, 2H; CH$_2$), 1.35 (t, $J = 7$ Hz, 3H; CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 166.8, 150.7, 131.6, 120.2, 113.8, 66.9, 22.3, 10.7; FTIR: ν = 3429, 3344, 3226, 2956, 2905, 1676, 1274, 1111, 850, 771 cm$^{-1}$.

Butyl 4-aminobenzoate, (B1d)

Aminobenzoic acid (5 g, 36mmol), n-butanol (200 mL, 2.1 mol), concentrated sulfuric acid (12 mL, 225 mmol) were used. Product: as white crystals; mp 57-58 °C, (4.5 g, yield 64%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.84 (d, $J = 8.7$ Hz, 2H; Ar H), 6.64 (d, $J = 8.7$ Hz, 2H; Ar H), 4.2 (q, $J = 7$ Hz, 2H), 4.1 (b, 2H, NH$_2$), 1.7 (m, $J = 7$ Hz, 2H), 1.45 (m, $J = 7$ Hz, 2H), 1.0 (t, $J = 7$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 166.9, 150.9, 131.6, 120.0, 113.8, 64.3 30.9, 19.3, 13.9; FTIR: ν = 3418, 3339, 3222, 2947, 1680, 1593, 1274, 1116, 770 cm$^{-1}$.

Isopropyl 4-aminobenzoate, (B1e)

This more difficult ester was synthesized using SOCl$_2$. Aminobenzoic acid (5 g, 36mmol), was dissolved in dry isopropanol (200 mL, 2.6 mol). SOCl$_2$ (15 mL, 206 mmol) was added slowly to the mixture. The resulting white slurry was refluxed overnight until clear. The cooled solution was added to aqueous saturated sodium bicarbonate. The product was extracted with ethyl acetate,
dried and isolated after removal of solvent in vacuo. No further purification was necessary. 

Product: as white crystals; mp 84-85 °C, (5.5 g, yield 84%). \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 7.84 (d, \(J = 8.7\) Hz, 2H; ArH), 6.64 (d, \(J = 8.7\) Hz, 2H; ArH), 5.2 (m, \(J = 6.2\) Hz, 1H), 4.1 (b, 2H, NH\(_2\)), 1.32 (d, \(J = 6.2\) Hz, 6H); \(^13\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 166.3, 150.7, 131.5, 120.5, 113.8, 67.6, 22.1; FT IR: \(\nu = 3446, 3348, 3224, 2976, 1684, 1666, 1592, 1276, 1104, 771\) cm\(^{-1}\).

**Tert-butyl 4-aminobenzoate**, (B1f)

This was the most difficult ester to synthesize, and was optimized by using SOCl\(_2\) as well. Aminobenzoic acid (3 g, 21.8 mmol) was mixed with SOCl\(_2\) (25mL, 344mmol) and refluxed for two hours until the acid dissolved and was converted to the acid chloride. The remaining SOCl\(_2\) was removed under vacuo. The remaining solid was melted (40 °C) and added dropwise to melted and stirring tert-butanol (100 mL, 1.1 mol) slowly and the resulting solution was refluxed for 1 hour. The cooled solution was added slowly to saturated sodium bicarbonate solution. The product was extracted with chloroform, dried, and the product was isolated after removing solvent under vacuo. The remaining white paste was triturated with hexanes and remaining white solid was filtered. No further purification was needed. Product: as white crystals; mp 107-108 °C, (3.2 g, yield 75%). \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 7.88 (d, \(J = 8.7\) Hz, 2H; ArH), 6.6 (d, \(J = 8.7\) Hz, 2H; ArH), 4.1 (b, 2H, NH\(_2\)), 1.55 (s, 9H); \(^13\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 166.0, 150.5, 131.5, 121.6, 113.7, 80.1, 28.4; FTIR: \(\nu = 3416, 3347, 3228, 2973, 1682, 1599, 1288, 1155, 1116, 772\) cm\(^{-1}\).

**Esterification Procedure for Remaining Phenyl Derivative and Substituted Phenyl Ester Precursors**

First, the p-nitro ester was synthesized using p-nitro benzoic chloride, followed by a reduction of the nitro group to the corresponding amino derivative. Synthesis of p-nitro ester precursors. (Adapted from Yokozawa)\(^{120}\)
Scheme B.2. Reaction scheme depicting esterification of 4-nitrobenzoyl chloride.

Phenyl 4-nitrobenzoate (B2g).

In one flask was placed phenol (3 g, 32.3 mmol), trimethylamine (TEA) (5 mL, 35.6 mmol), and DCM (50 mL). In a separate flask was placed 4-nitrobenzoyl chloride (6 g, 32.3 mmol) and 20 mL of DCM. The dissolved acid chloride was slowly added to the chilled, stirring phenol solution. The resulting solution was stirred at room temperature for 3 hours. The ester was isolated by pouring the solution into saturated bicarbonate, and extraction with dichloromethane. The organic layer was then washed with aqueous sodium hydroxide and brine. After solvent was removed in vacuo, the product obtained without further purification. Product: as white crystals; mp 128-129 °C, (6.5 g, yield 83%). \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 8.37 (dd, 4H, Ar H), 7.46 (t, \(J = 8\) Hz, 2H, Ar H), 7.3 (t, \(J = 8\) Hz, 1H, Ar H), 7.2 (d, \(J = 8\) Hz, 2H, Ar H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 163.4, 151.0, 150.5, 135.0, 131.5, 129.8, 126.5, 123.7, 121.5; FTIR: \(\nu = 3150, 1737, 1518, 1265, 1181, 1077, 755, 708\) cm\(^{-1}\).

P-tolyl 4-nitrobenzoate (B2h)

P-cresol (2.91 g, 26.9 mmol), TEA (4.1 mL, 26.6 mmol), 4-nitrobenzoyl chloride (5 g, 26.9 mmol). Product: as white crystals; mp 97-98 °C, (6.2 g, yield 90%). \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)): 
8.37 (dd, 4H, ArH), 7.24 (d, J = 8.8 Hz, 2H, ArH), 7.1 (t, J = 8.8 Hz, 2H, ArH), 2.38 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 163.6, 150.9, 148.3, 136.2, 135.2, 131.4, 130.3, 123.8, 121.2, 21.1; FTIR: ν = 3150, 1725, 1526, 1505, 1272, 1199, 1088, 871, 850, 739, 708 cm$^{-1}$.

**P-(tert-butyl)phenyl 4-nitrobenzoate (B2i)**

P-(tert-butyl)phenol (4.04 g, 26.93 mmol), TEA (4.1 mL, 26.6 mmol), 4-nitrobenzoyl chloride (5 g, 26.9 mmol). Product: as white crystals; mp 104-105 °C, (7.2 g, yield 89%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.37 (dd, 4H, ArH), 7.46 (d, J = 8.4 Hz, 2H, ArH), 7.15 (t, J = 8.4 Hz, 2H, ArH), 1.34 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 163.5, 150.8, 149.4, 148.2, 135.2, 131.4, 126.6, 123.7, 120.7, 34.6, 31.5; FTIR: ν = 2966, 2871, 1731, 1520, 1268, 1197, 1170, 1072, 714 cm$^{-1}$.

**P-methoxyphenyl 4-nitrobenzoate (B2j)**

P-methoxyphenol (3.34 g, 26.93 mmol), TEA (4.13 mL, 26.62 mmol), 4-nitrobenzoyl chloride (5 g, 26.9 mmol). Product: as white crystals; mp 114-115 °C, (6.5 g, yield 88%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.37 (dd, 4H, ArH), 7.14 (d, J = 9 Hz, 2H, ArH), 6.95 (t, J = 9 Hz, 2H, ArH), 3.83 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 163.7, 157.7, 150.9, 144.0, 135.1, 131.4, 123.7, 122.3, 114.7, 55.7; FTIR: ν = 2966, 2871, 1731, 1520, 1345, 1190, 1014, 802, 708 cm$^{-1}$.

**P-trifluoromethyl phenyl 4-nitrobenzoate (B2k)**

P-trifluoromethyl phenol (4.37 g, 26.9 mmol), TEA (4.1 mL, 26.6 mmol), 4-nitrobenzoyl chloride (5 g, 26.9 mmol). Product: as white crystals; mp 85-86 °C, (7.5 g, yield 89%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.37 (s, 4H, ArH), 7.73 (d, J = 8.6 Hz, 2H, ArH), 7.37 (t, J = 8.6 Hz, 2H, ArH); $^{13}$C NMR (125 MHz, CDCl$_3$, δ): 162.8, 152.9, 151.1, 134.3, 131.5, 127.1 (q, J = 3.4 Hz, C-F), 124.9, 124.0, 122.7, 122.1; FTIR (ATR): ν = 3117, 1743, 1609, 1522, 1264, 1102, 1059, 854, 713 cm$^{-1}$ (m);
Reduction of p-Nitro Ester Precursors to Amino Derivatives. (Adapted from Yokozawa)\textsuperscript{120}

Scheme B.3. Reaction scheme depicting the reduction of p-nitro group to yield the amino functionality necessary for alkylation.

Phenyl 4-aminobenzoate (B3g) representative procedure

Phenyl 4-nitrobenzoate (5 g, 20.6 mmol) was placed in a roundbottom flask with Pd/C (100 mg), ethyl acetate (100 mL), a stir bar and capped with a septa. The atmosphere was replaced with hydrogen, and stirred overnight. The Pd/C was then filtered off and the solvent was removed in vacuo. The product was obtained without further purification with quantitative yield. Product: as white crystals; mp 171-172 °C. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, δ): 8.0 (d, J = 8.6 Hz, 2H, ArH), 7.4 (t, J = 8 Hz, 2H, ArH), 7.2 (t, J = 7.8 Hz, 1H, ArH), 7.2 (d, J = 8 Hz, 2H, ArH), 4.2 (b, 2H NH\textsubscript{2}); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, δ): 165.4, 151.5, 151.2, 132.5, 129.5, 125.7, 122.0, 118.7, 113.9; FTIR (ATR): ν = 3411, 3338, 3232, 1697, 1636, 1592, 1279, 1191, 1166, 1068, 741 cm\textsuperscript{-1}.

P-tolyl 4-aminobenzoate (B3h)

p-tolyl 4-nitrobenzoate (4g, 26.93mmol), TEA (4.13mL, 26.62mmol), 4-nitrobenzoyl chloride (5g, 26.9mmol). Product: as white crystals; mp 162-163 °C. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, δ): 8.0 (d, J = 8.6 Hz, 2H, ArH), 7.2 (d, J = 8.2 Hz, 2H, ArH), 7.05 (d, J = 8.2 Hz, 2H, ArH), 6.68 (d, J = 8.2 Hz, 2H, ArH), 4.15 (b, 2H NH\textsubscript{2}) 2.36 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, δ): 165.4, 151.4, 149.0,
135.2, 132.3, 130.0, 121.6, 119.0, 113.8, 21.0; FTIR (ATR): $\nu = 3418, 3335, 3226, 1698, 1593, 1514, 1277, 1197, 1159, 845, 765, 696 \text{ cm}^{-1}$.

P-(tert-butyl)phenyl 4-aminobenzoate (B3i)

P-(tert-butyl)phenol (4.04g, 26.93mmol), TEA (4.13mL, 26.62mmol), 4-nitrobenzoyl chloride (5g, 26.9mmol). Product: as white crystals; mp 193-195 °C. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.0 (d, $J = 8.6$ Hz, 2H, ArH), 7.4 (d, $J = 8.2$ Hz, 2H, ArH), 7.1 (d, $J = 8.2$ Hz, 2H, ArH), 6.7 (d, $J = 8.2$ Hz, 2H, ArH), 4.15 (b, 2H NH$_2$), 1.33 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 165.5, 141.5, 148.8, 148.4, 132.4, 126.3, 121.3, 119.0, 113.9, 34.6, 31.6; FTIR (ATR): $\nu = 3466, 3370, 3229, 2963, 1679, 1588, 1516, 1274, 1159, 1063, 768, 614 \text{ cm}^{-1}$.

P-methoxyphenyl 4-aminobenzoate (B3j)

P-methoxyphenol (3.34 g, 26.93 mmol), TEA (4.13 mL, 26.62 mmol), 4-nitrobenzoyl chloride (5 g, 26.9 mmol). Product: as white crystals; mp 177-178 °C. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.0 (d, $J = 8.6$ Hz, 2H, ArH), 7.09 (d, $J = 8.2$ Hz, 2H, ArH), 6.91 (d, $J = 8.2$ Hz, 2H, ArH), 6.68 (d, $J = 8.2$ Hz, 2H, ArH), 4.15 (b, 2H NH$_2$), 3.81 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 165.6, 157.1, 151.4, 144.7, 132.3, 122.7, 118.9, 114.5, 113.9, 55.7; FTIR (ATR): $\nu = 3462, 3369, 3253, 1700, 1643, 1593, 1503, 1272, 1157, 1023, 869, 843, 802, 762 \text{ cm}^{-1}$.

P-trifluoromethyl phenol 4-aminobenzoate (B3k)

Product: as white crystals; mp 175-177 °C. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.0 (d, $J = 8.6$ Hz, 2H, ArH), 7.66 (d, $J = 8.6$ Hz, 2H, ArH), 7.31 (d, $J = 8.6$ Hz, 2H, ArH), 6.7 (d, $J = 8.6$ Hz, 2H, ArH), 4.2 (b, 2H NH$_2$); $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 164.7, 153.9, 151.8, 132.6, 126.8 (q, $J = 3.7$ Hz), 125.2, 122.5, 118.1, 113.9, 99.9; $^{19}$F NMR 1 peak; FTIR (ATR): $\nu = 3509, 3390, 3224, 1711, 1627, 1598, 1163, 1050, 844, 763 \text{ cm}^{-1}$;
Precursors to synthesis of DMA-P initiator


**Diphenyl Terephthalate (B4a)**

Terephthaloyl chloride (6 g, 29.9 mmol) and phenol (6.2 g, 65.9 mmol) were placed in a 250mL roundbottom flask and dry THF (100mL) was added. After fully dissolved, triethylamine (10.4 mL, 74.9mmol) was added slowly to stirring mixture. The solution was then stirred at room temperature for 1 hour. The resulting precipitate was filtered and washed with fresh THF. The residue was added to water, stirred for 1 hour and filtered again. The collected product was dried in vacuum oven at 60°C for 4 hours to yield the pure product, diphenylterphthalate. Product: as white crystals; mp 199-200°C, (9.2g, yield 97%). $^1$H NMR (500 MHz, DMSO-D6, δ): 8.29 (s, 4H, Ar H), 7.46 (t, $J = 8.2$ Hz, 4H; CH$_2$), 7.31 (m, 6H); $^{13}$C NMR (125 MHz, DMSO-D6, δ): 164.4, 151.0, 134.0, 130.8, 130.2, 126.8, 122.4; FTIR (ATR): $\nu = 3059, 1729, 1485, 1266, 1076, 915, 738, 717, 688$ cm$^{-1}$. 

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Monophenyl terephthalate (4-(phenoxy carbonyl)benzoic acid) (B4b) Reaction adopted from chase.²³⁴

Diphenyl terephthalate (4.4g, 13.82 mmol) was stirred in a 250mL roundbottom flask with liquid tert-butanol (300mL) and heated until boiling and solute dissolves. A separate aqueous solution of KOH was prepared by adding KOH pellets (1.01g, 17.9mmol, near 138.8mmol, when counting water content) to 10 mL of DI water. The KOH solution was added to the diphenyl/tert-butanol solution and resulting solution was refluxed for 1 hour. The product was isolated by cooling the mixture and pouring into DI water (1L) and acidified with concentrated HCl until pH = 3, causing a white precipitate to form. The product was collected by filtration, washed with DI water and recrystallized from boiling EtOH:H₂O 50:50. Product: as white crystals; mp 240-241 °C, (0.86 g, yield 70%). ¹H NMR (500 MHz, DMSO-D6, δ): 13.4 (b, 1H, COOH), 8.2 (d, J = 8.5 Hz, 2H, Ar H), 8.1 (d, J = 8.5 Hz, 2H, Ar H), 7.45 (t, J = 8 Hz, 2H, Ar H), 8.28 (d, t, J = 8 Hz, 3H, Ar H); ¹³C NMR (125 MHz, CDCl₃, δ): 167.4, 164.5, 151.0, 135.9, 133.0, 130.5, 130.3, 130.2, 126.7, 122.4; FTIR (ATR): ν = broad (2885, 2770, 2550), 1736, 1682, 1427, 1246, 1186, 1163, 1075, 944, 723, 698 cm⁻¹.
**APPENDIX C**

**Initiator Precursor Synthesis**

*Precursors to synthesis of DMA-P initiator – See Appendix B*

*Precursors Used in Synthesis of Substituted Phenyl DMA Initiator*

Methyl 4-(dimethylcarbamoyl)benzoate (C1a)

4-(methoxycarbonyl)benzoic acid (6.8g, 38mmol) was refluxed with thionyl chloride (20mL, 280mmol) for two hours. Excess thionyl chloride was removed under vacuum leaving the acid chloride. The resulting solid was dissolved in dichloromethane (50 mL). Triethylamine (5.8mL, 41.7mmol) was added to the stirring solution. Dimethylamine (2M, THF) was then added dropwise (22.7mL, 45.5mmol) and resulting solution was refluxed for 1 hour. The solution was cooled to room temperature and solvent was removed to leave the product and ammonium salt. The product was dissolved in ethyl acetate and filtered through a short silica column. The solvent was then removed and the resulting product was dried to leave pure off-yellow crystalline solid (7.8g, yield 97%). m.p. 108-109 °C, (1.1 g, yield: 91%). $^1$H NMR (500 MHz, CDCl$_3$, 25°C): $\delta$ = 8.06 (d, $J$
= 8.32 Hz, 2H), 7.47 (d, J = 8.32 Hz, 2H), 3.92 (s, 1H), 3.11 (br, 3H), 2.94 (br, 3H); 13C NMR (125 MHz, CDCl₃) 170.5, 166.5, 140.7, 131.0, 129.7, 127.2, 52.4, 39.4, 35.3 ppm; IR (ATR): 2951, 2853, 1721, 1618, 1277, 1257, 1109, 1078, 726 cm⁻¹.

4-(dimethylcarbamoyl)benzoic acid (C1b)

Methyl 4-(dimethylcarbamoyl)benzoate (S2a) (3g, 14.5mmol) was dissolved in methanol (100ml). LiOH, monohydrate (6.08g, 144.8mmol) was added and dissolved solution was stirred for 1 hour. The solvent was then removed under vacuum. The residue was then dissolved in DI water and poured into a beaker. The product was precipitated by titrating the solution with concentrated HCl until the pH reached 3. The product was then extracted with ethyl acetate, dried over magnesium sulfate, and rotovapped and dried in oven. Product: as off yellow powder: m.p. 174-176 °C, (2.56 g, yield 91%). ¹H NMR (500 MHz, CDCl₃, δ): 13.1 (b, 1H, COOH), 7.9 (d, J = 8.5 Hz, 2H, ArH), 7.45 (d, J = 8.5 Hz, 2H, ArH), 3.11 (br, 3H), 2.94 (br, 3H); 13C NMR (125 MHz, CDCl₃) 170.5, 166.5, 140.7, 131.0, 129.7, 127.2, 52.4, 39.4, 35.3 ppm; IR (ATR): 3000 br, 2951, 2853, 1721, 1618, 1277, 1257, 1109, 1078, 726 cm⁻¹.